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DEVELOPMENT OF OXIDATION RESISTANT  
COATINGS FOR USE ABOVE 3500°F

By P. F. Campbell, K. A. Gebler, and M. H. Ortner

September 1965

Prepared Under Contract No. NAS9-3413

by

VITRO LABORATORIES  
West Orange, New Jersey

[REDACTED]

Manned Spacecraft Center

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

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## FOREWORD

This is the Final Report under NASA Contract NAS9-3413 and covers the work performed during the period 7 August 1964 through 7 September 1965 on the development of oxidation resistant coatings for the protection of tantalum-base alloys at temperatures above 3500°F.

This program was accomplished under the technical direction of Mr. T. A. Clancy of the Structures and Mechanics Division, Manned Spacecraft Center, National Aeronautics and Space Administration.

This report has been assigned Vitro Laboratories' internal number VL-2382-13-O.

In addition to the authors, those contributing to the performance of this program at Vitro included Dr. S. Grand, Department Head, and Messrs. R. Armswood and R. Sonner, Research Technicians.

## 1. INTRODUCTION AND PROGRAM OBJECTIVES

This is the Final Report on NASA Contract NAS9-3413 covering the period 7 August 1964 - 7 September 1965. Work under this contract was performed for the NASA Manned Spacecraft Center, Spacecraft Materials Branch, Structures and Mechanics Division. Mr. Tim Clancy of the Structures and Mechanics Division was the NASA Project Engineer.

The objective of this program was the development of oxidation resistant coatings for use above 3500°F. All coatings studied in the course of the program were formed by electrophoretic deposition since this is a flexible and rapid means of screening a variety of candidate systems and since this coating technique lends itself readily to the formation of uniformly gradated multicomponent systems.

The premise upon which this program was based was that oxidation protection of refractory alloys at temperatures above 3500°F will most likely be accomplished with refractory ceramic oxides which do not melt at this temperature. The refractory oxides, however, cannot be directly deposited in useful form on a refractory metal since no mechanism for bonding to the substrate (i. e., solid solution, chemical displacement) is available, and because the difference of thermal expansion between the oxide and the metal leads to cracking of the coating upon cooling from the sintering temperature. For these reasons, systems were studied in which an intermetallic compound having: (a) a high melting point, (b) good inherent oxidation resistance and diffusional stability, and (c) a coefficient of thermal expansion intermediate between that of the oxide and the substrate, was used to form a gradated bonding layer between the alloy to be protected and the oxide protective layer.

## 2. MATERIALS AND EQUIPMENT

### 2.1 Physical Properties and Analysis of Coating Materials

In this section a review is presented of the properties of the coating and substrate materials selected for study in this program. Table 1 shows selected physical properties for a number of compounds studied in this program, while Table 2 summarizes the sources of supply from which these materials were obtained. Tables 3-7 give the results of chemical analysis of the same powders.

TABLE 1

SELECTED PHYSICAL PROPERTIES OF  
VARIOUS OXIDES AND INTERMETALLIC COMPOUNDS

	<u>M.P. (°F)</u>	<u>Density (g/cc)</u>	<u>Knoop Microhardness 100 g load (kg/mm<sup>2</sup>)</u>	<u>Thermal Expan- sion per °F × 10<sup>6</sup></u>
Al <sub>2</sub> O <sub>3</sub>	3720	3.96	2260	4.7 (to 1500°F)
ZrO <sub>2</sub> (cubic)	4760	5.6 - 6.26	900	4.7 (to 3800°F)
CaZrO <sub>3</sub>	4170	4.78	-	6.4 (to 2400°F)
SrZrO <sub>3</sub>	4900	5.48	-	5.34 (to 1830°F)
MoSi <sub>2</sub>	3690	6.24	1260	4.5 (to 2600°F)
TaSi <sub>2</sub>	4350	9.1	1200	4.7 (to 2600°F)
90ZrB <sub>2</sub> -10MoSi <sub>2</sub>	> 4280	6.12 (calc.)	1500	3.9
Ta <sub>2</sub> Be <sub>17</sub>	3610	5.05	1120*	8.72 (to 2750°F)
TaAl <sub>3</sub>	4950	6.92	-	6.5
Ta-10W Alloy	5495	16.9	230 (annealed)	3.9 (1600°-2200°F)
WSi <sub>2</sub>	3840	9.87	1090	4.6 (to 1830°F)

\*Vickers Hardness, 2.5 kg load

TABLE 2  
EXPERIMENTAL MATERIALS

<u>Compound</u>	<u>Source and Form</u>
3.5% CaO-Stabilized, HfO <sub>2</sub> -Free Zirconia	Zirconium Corp. of America, Grade CH nominal 5 micron powder
8% Y <sub>2</sub> O <sub>3</sub> -Stabilized Zirconia	Zirconium Corp. of America, nominal 5 micron powder
CaZrO <sub>3</sub>	Zirconium Corp. of America, nominal 5 micron powder
SrZrO <sub>3</sub>	Zirconium Corp. of America, -325 mesh powder
TaSi <sub>2</sub>	A. D. Mackay, -150 +325 mesh powder, 99+ % pure
Al <sub>2</sub> O <sub>3</sub> (alpha)	Linde Type A, 0.3 micron powder, 99.98+ % pure
MoSi <sub>2</sub>	Shieldalloy 3 micron powder
ZrB <sub>2</sub>	A. D. Mackay, -200 mesh powder, 99+ % pure
Ta <sub>2</sub> Be <sub>17</sub>	Brush Beryllium, -200 mesh powder
WSi <sub>2</sub>	Shieldalloy, -325 mesh, 99% purity

TABLE 3  
TYPICAL ANALYSES OF ZIRCONIUM COMPOUNDS

<u>3.5%Calcia- Stabilized Zirconia</u>		<u>8% Y<sub>2</sub>O<sub>3</sub>- Stabilized Zirconia</u>		<u>Calcium Zirconate</u>	<u>Strontium Zirconate</u>
Al	200 ppm	ZrO <sub>2</sub>	91.8%*		Al <sub>2</sub> O <sub>3</sub> 0.1%
B	1	Y <sub>2</sub> O <sub>3</sub>	8%**	CaZrO <sub>3</sub> > 99%	SiO <sub>2</sub> 0.1%
Cd	0.5	SiO <sub>2</sub>	0.2%	SiO <sub>2</sub> < 0.5%	CaO 0.9%
Cl	10	Al <sub>2</sub> O <sub>3</sub>	0.1%	L. O. I. < 1%	BaO 1.7%
Cr	50				SrZrO <sub>3</sub> Balance*
Co	1				
Cu	25				
Fe	500			*ZrO <sub>2</sub> impurities shown in Column 1	
Hf	100				
Pb	5				
Mg	200			**Y <sub>2</sub> O <sub>3</sub> is commercial grade, containing about 10% rare earths, compatible with ZrO <sub>2</sub>	
Mn	10				
Ni	10				
Si	1500				
Ti	150				
(SO <sub>4</sub> )	500				



TABLE 4  
SPECTROGRAPHIC ANALYSES OF MoSi<sub>2</sub> AFTER DILUTE HCl LEACH

<u>Impurity</u>	<u>%</u>	<u>Impurity</u>	<u>%</u>
Al	0.05	Ni	0.001
B	0.005	Sn	0.001
Ba	0.005	Ti	0.003
Ca	0.2	V	0.01
Co	0.005		
Cr	0.02		
Cu	0.007		
Fe	0.1		
Mg	0.005		
Mn	0.005		

Ag, Be, Bi, Ga, In, Pd, Sr, Zr - Not detected, <0.001%

As, Au, Cd, Hf, Ir, Li, Na, Os, Ru, Sb, Ta, W - Not detected, < 0.05%

Ge, Cb, Pb, Rh, Pt - Not detected, <0.005%

TABLE 5

## SPECTROGRAPHIC ANALYSIS OF ZIRCONIUM DIBORIDE POWDER

<u>Impurity</u>	<u>%</u>	
Ca	0.005	Not Detected, <0.005% - Ag, Al, Ba, Be, Bi, Cu, Ga, In, Mg, Ni, Pd, Sn, Sr, V, Cb, Pb, Pt, Rh, Ge
Co	0.02	
Cr	0.01	
Fe	0.07	
Hf	1	
Mn	0.001	Not Detected, <0.05% - As, Au, Cd, Ir, Li, Na, Os, Ru, Sb, Ta, Tl, W, Zn
Mo	0.02	
Si	0.003	
Ti	0.05	

TABLE 6  
SPECTROGRAPHIC ANALYSIS OF  
TUNGSTEN DISILICIDE POWDER (SOURCE "A")

---

SILVER -----	ND<0.001%
ALUMINUM-----	0.07%
ARSENIC-----	ND<0.05%
GOLD-----	ND<0.05%
BORON-----	0.01%
BARIUM-----	ND<0.001%
BERYLLIUM-----	ND<0.001%
BISMUTH-----	ND<0.001%
CALCIUM-----	0.03%
CADIUM-----	ND<0.05%
COBALT-----	0.001%
CHROMIUM-----	0.007%
COPPER-----	0.005%
IRON-----	0.1%
GALLIUM-----	ND<0.001%
GERMANIUM-----	ND<0.005%
HAFNIUM-----	ND<0.05%
INDIUM-----	ND<0.001%
IRIDIUM-----	ND<0.05%
LITHIUM-----	ND<0.05%
MAGNESIUM-----	0.007%
MANGANESE-----	0.005%
MOLYBDENUM-----	0.05%
SODIUM-----	ND<0.05%
COLUMBIUM-----	ND<0.005%
NICKEL-----	0.005%
OSMIUM-----	ND<0.05%
LEAD-----	ND<0.003%
PALLADIUM-----	ND<0.001%
PLATINUM-----	ND<0.005%
RUTHENIUM-----	ND<0.05
RHODIUM-----	ND<0.005%
ANTIMONY-----	ND<0.05%
SILICON-----	High
TIN-----	ND<0.001%
STRONTIUM-----	ND<0.001%
TANTALUM-----	ND<0.05%
TELLURIUM-----	ND<0.1%

TABLE 6 (Continued)

THALLIUM-----	ND<0.01%
TITANIUM-----	0.02%
VANADIUM-----	0.001%
TUNGSTEN-----	High
ZINC-----	ND<0.03%
ZIRCONIUM-----	0.005%

\*                      \*                      \*

(ND< - Not Detected Less Than)

TABLE 7  
ANALYSIS OF  
TUNGSTEN DISILICIDE POWDER  
(SOURCE "B")

W	76.0 %
Si	23.4
C	00.12
Fe	00.15
O	00.20
	<hr/>
	99.87%

Since tantalum aluminide was not available commercially in powder form, the compound was synthesized at Vitro. X-ray diffraction analysis showed that the only identifiable phase was  $\text{TaAl}_3$  with "d" spacings comparable to the ASTM standard.

## 2.2 Gradated Coating Equipment

### 2.2.1 Description

The gradated coatings used in this program were deposited with a special Vitro-designed pumping system operating in conjunction with an electrophoretic cell. The pumping system is shown in Figure 1, and a photograph of the pumps combined with typical electrophoretic deposition equipment is shown in Figure 2.

The pumping system, designed to feed a 2-component, continuously varied electrophoretic dispersion to the coating vessel, consists of two Sigma-motor Type T-8 tubing pumps driven by a 1/2 hp, 1800 rpm motor which is coupled to the pumps through a Vickers variable speed reducer and two Graham variable speed drives connected in opposition. The maximum pumping speed of the T-8 pumps is set by the output rpm of the Vickers control. The function of the two variable speed cross-linked drives is to vary the speed of one tubing pump from 5%-100% of the maximum rpm while the other pump operates between 100% and 5% of the maximum. The period of the coating run was adjusted by connecting a motorized drive and timing switch to the control on the Graham drives.

A calibration curve which gives the variation in composition of the pump effluents as a function of the setting of the control on the Graham drives, is shown in Figure 3. The curve is almost linear over the range of the control and its shape invariant at input pumping speeds ranging from 210-1620 rpm when pumping a fluid mixture containing 60 vol. % isopropanol-40 vol. % nitromethane.

Measurement of the total volumetric flowrate obtained at various input speeds and vernier settings indicated that at each input speed the flowrate was constant over the middle of the range of the vernier and increased slightly at the low end and high end of the range. This variation was probably due to small discrepancies between the pumping rates of the individual tubing pumps.

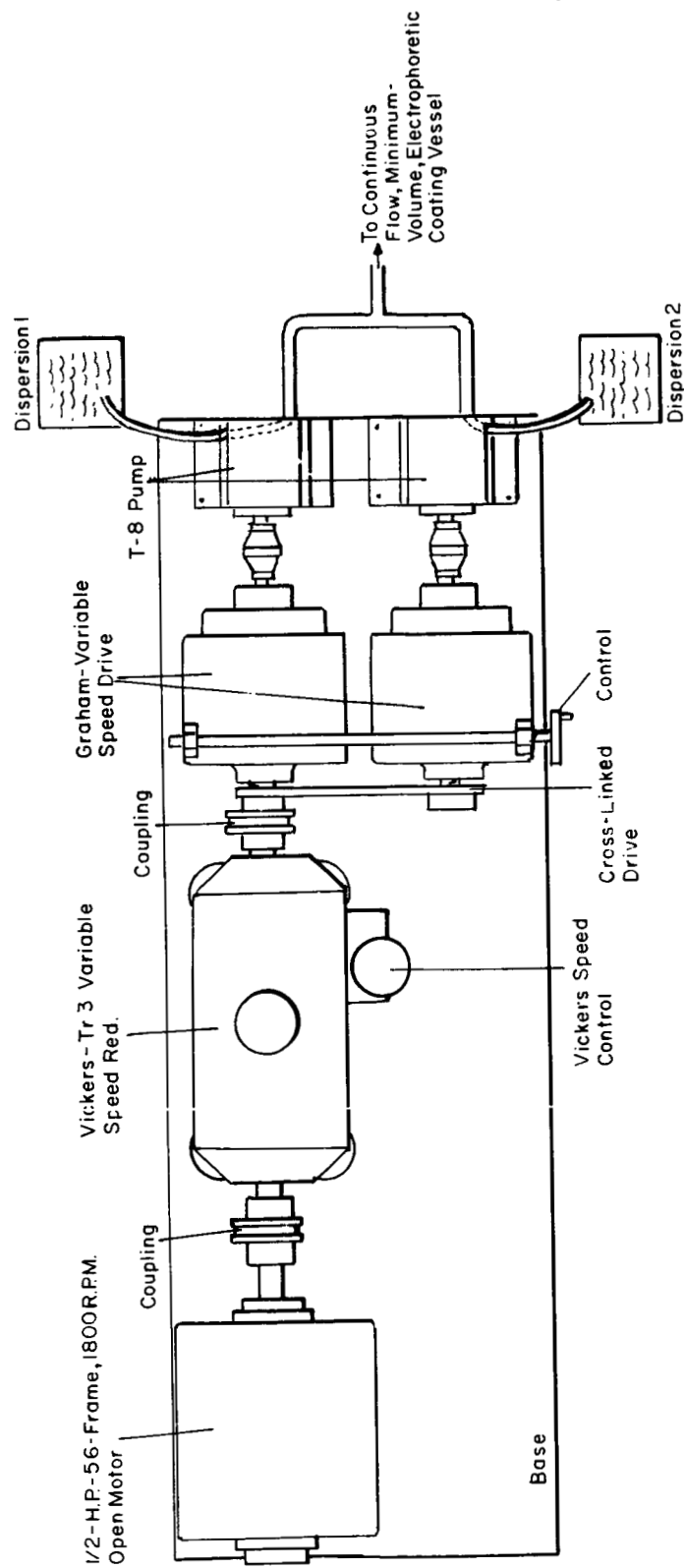


FIGURE 1  
PUMPING SYSTEM FOR ELECTROPHORETIC  
DEPOSITION OF GRADATED COATINGS

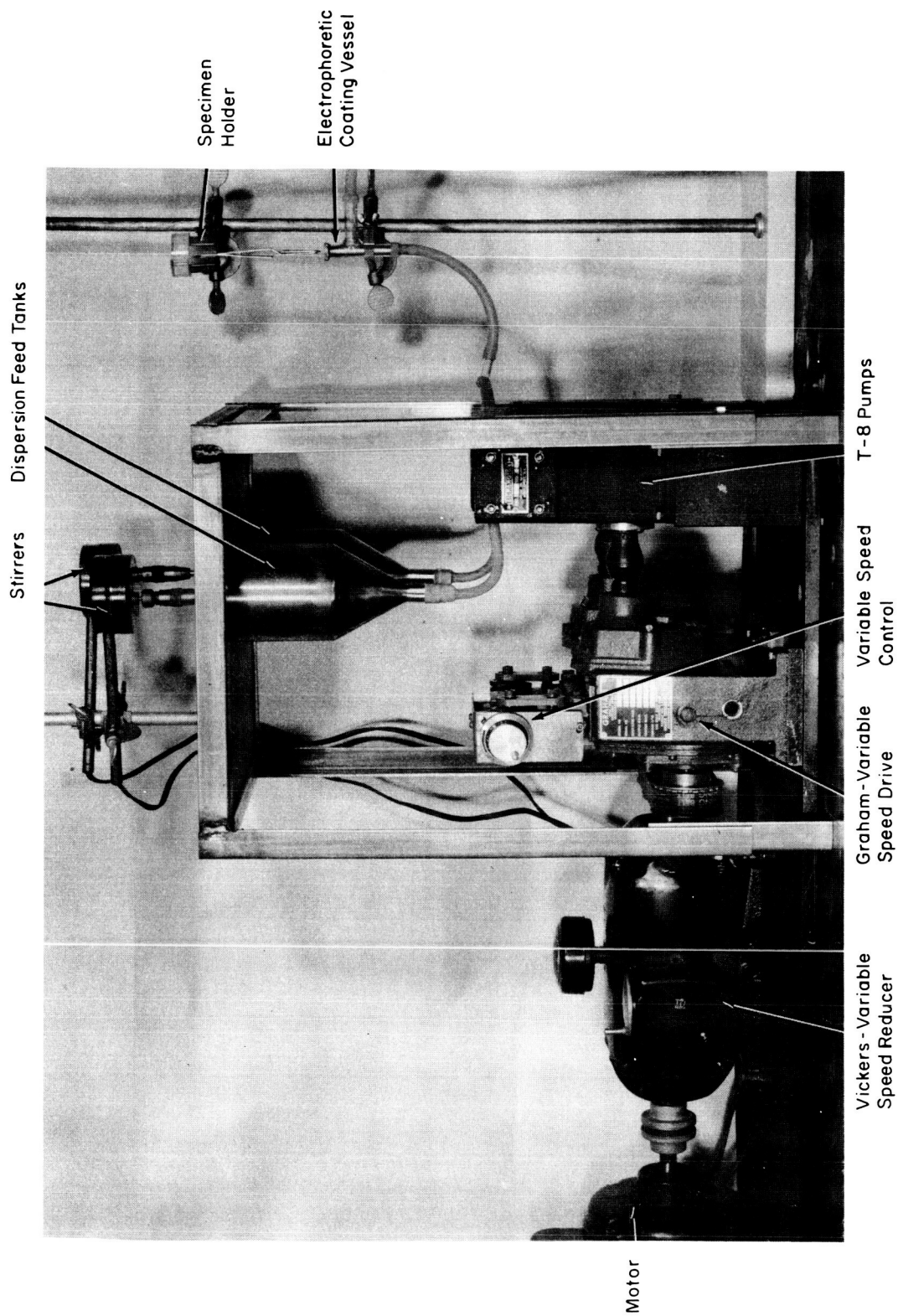


FIGURE 2

PHOTOGRAPH OF PUMPING SYSTEM FOR  
ELECTROPHORETIC DEPOSITION OF GRADATED COATINGS

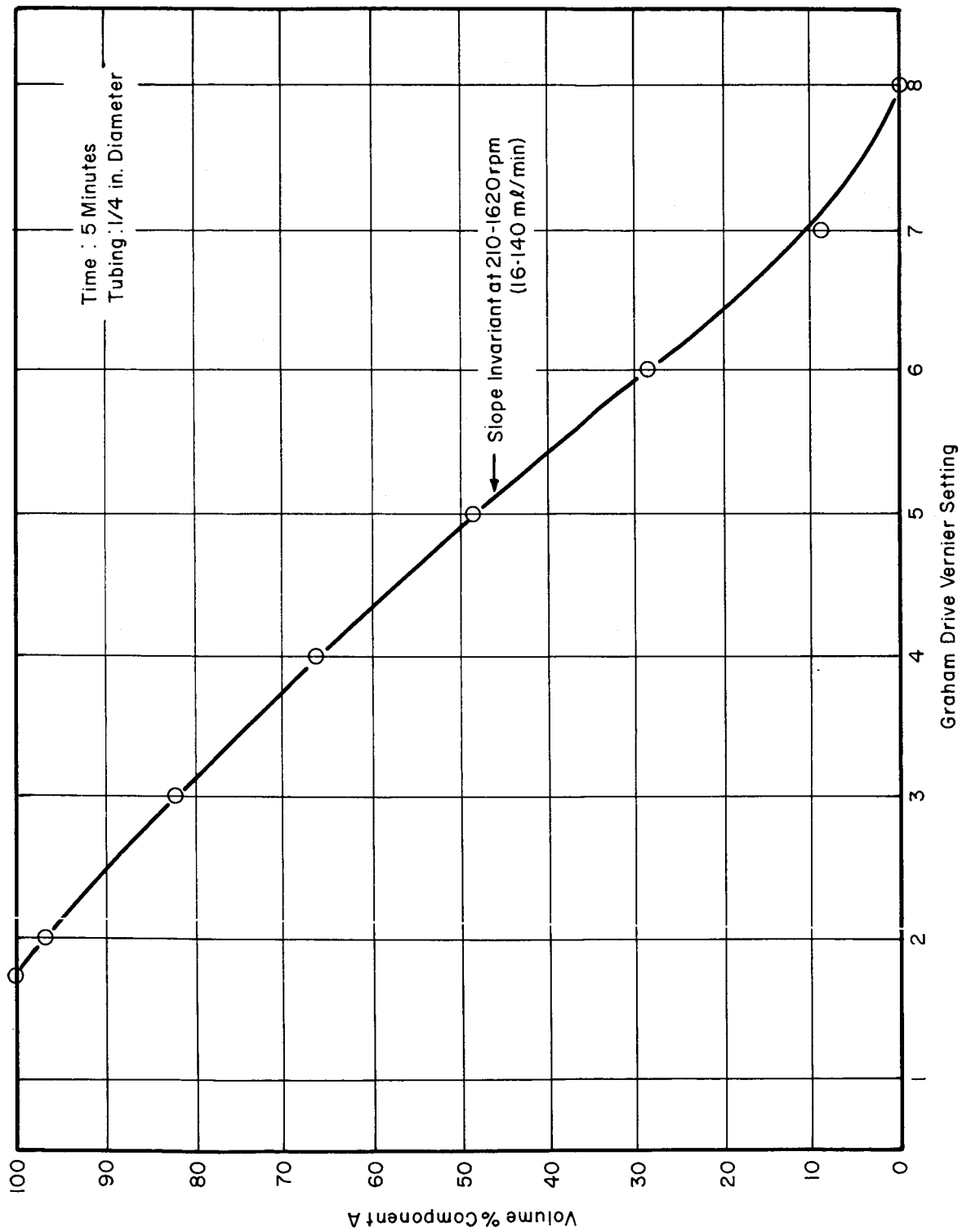


FIGURE 3  
EFFLUENT COMPOSITION VS. PUMPING SPEED



An electrophoretic cell for coating panel specimens was tested and found to be satisfactory. This cell has inside dimensions of  $1/2'' \times 1''$  and is  $1-1/2''$  deep. It is suitable for coating specimens which are  $.020'' \times 1/2'' \times 1-1/4''$ . Figure 4 is a sketch of this cell. In operation, the dispersion enters at the bottom and flows upward past the specimen. At the top of the cell the bulk of the dispersion enters horizontal recirculation channels which carry it back to the pumps for further mixing. The remainder of the dispersion overflows to a waste collecting vessel.

### 2.2.2 Coating Rate Studies

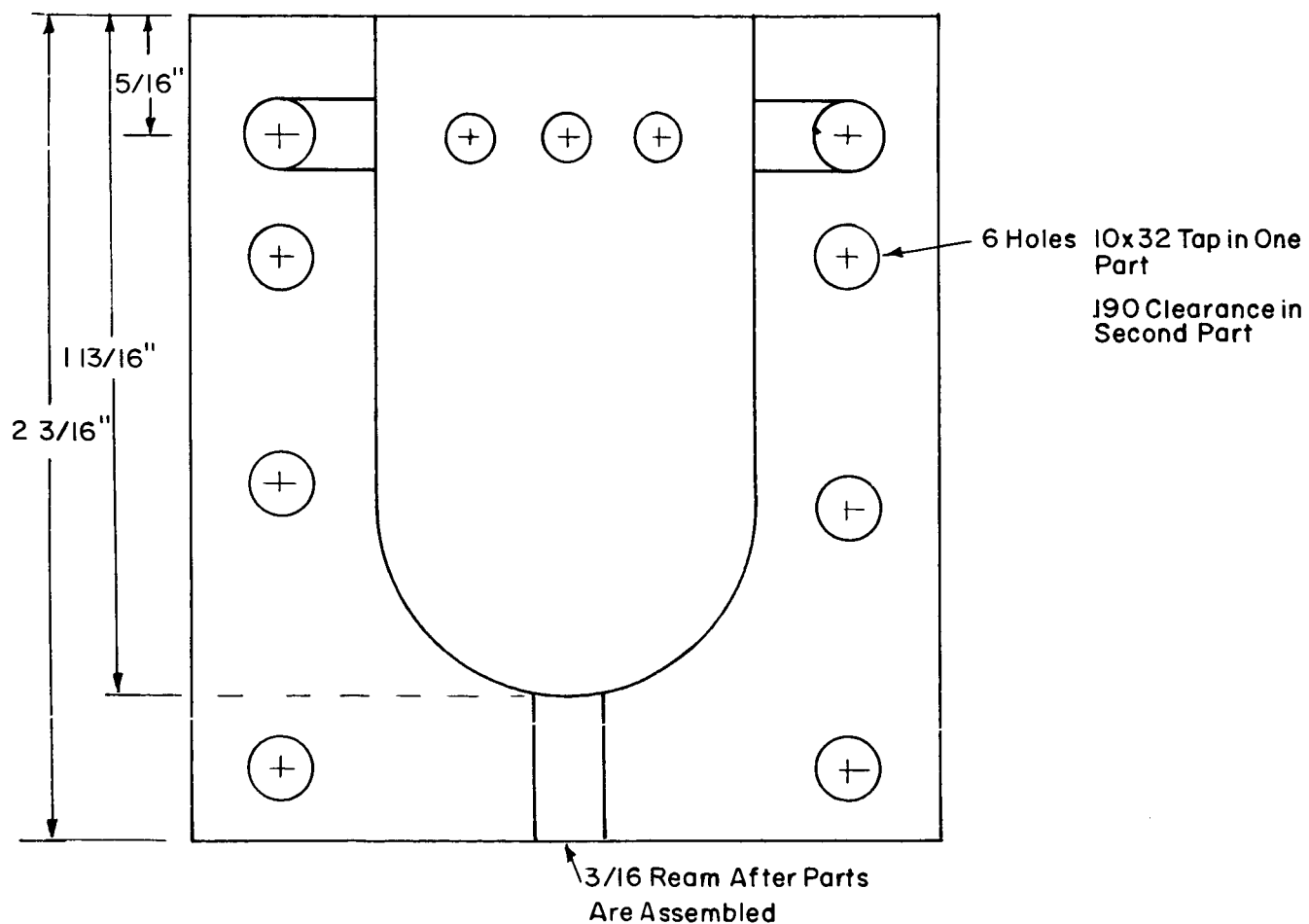
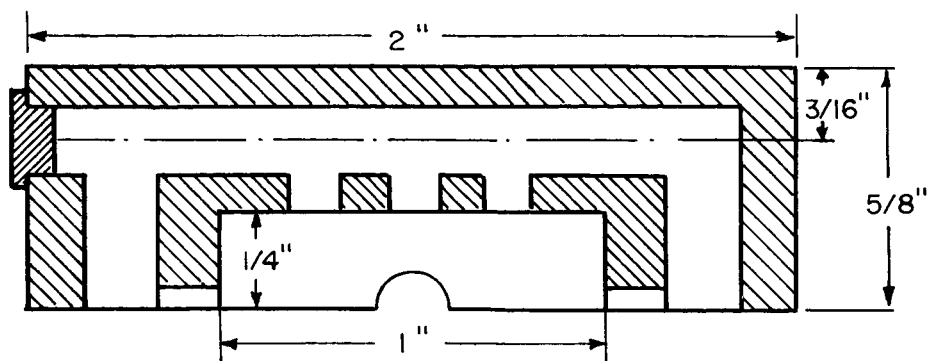
In order to evaluate the effectiveness of the deposition equipment in providing a gradated coating, preliminary experiments were made by depositing a mixture of oxide and nickel oxide powders on Kovar and copper wires, and subsequently hydrogen reducing and sintering the gradated deposit. A gradation of color was observed with the copper-nickel gradated coating and chemical analyses showed a uniform change from one metal to the other.

In subsequent experiments on the deposition of oxides and intermetallics, it was shown that in order to prepare uniformly gradated coatings from two dispersions of different compounds at the same concentration, it is necessary that the coating rates of the individual dispersions be equal or nearly equal. The coating rates of dispersions containing one weight percent of  $90\text{ZrB}_2$ - $10\text{MoSi}_2$ ,  $\text{WSi}_2$ ,  $8\%\text{Y}_2\text{O}_3$ -stabilized  $\text{ZrO}_2$ ,  $3.5\%\text{CaO}$ -stabilized zirconia,  $\text{SrZrO}_3$ , and  $\text{CaZrO}_3$  were investigated.

The dispersions were prepared as follows:

-325 mesh solids	8.5 grams
60% isopropanol-40% nitromethane	850 ml
Zein binder solution	6 ml
Electrolyte solution	0.5 ml

Steel panels were coated from these dispersions at 200 and 300 volts for periods of  $1/4$ ,  $1/2$ , 1, 2, 3, and 4 minutes, and the coating thickness and weight increase was recorded as a function of time. The results are shown in Figures 5 and 6. It may be seen that the coating rates of the  $\text{MoSi}_2$  and calcia-stabilized zirconia dispersions were lower than those of the other materials. Modifications of the particle size of these



2 Pieces Required Material - Brass

FIGURE 4  
ELECTROPHORETIC COATING  
CELL FOR SMALL COUPONS

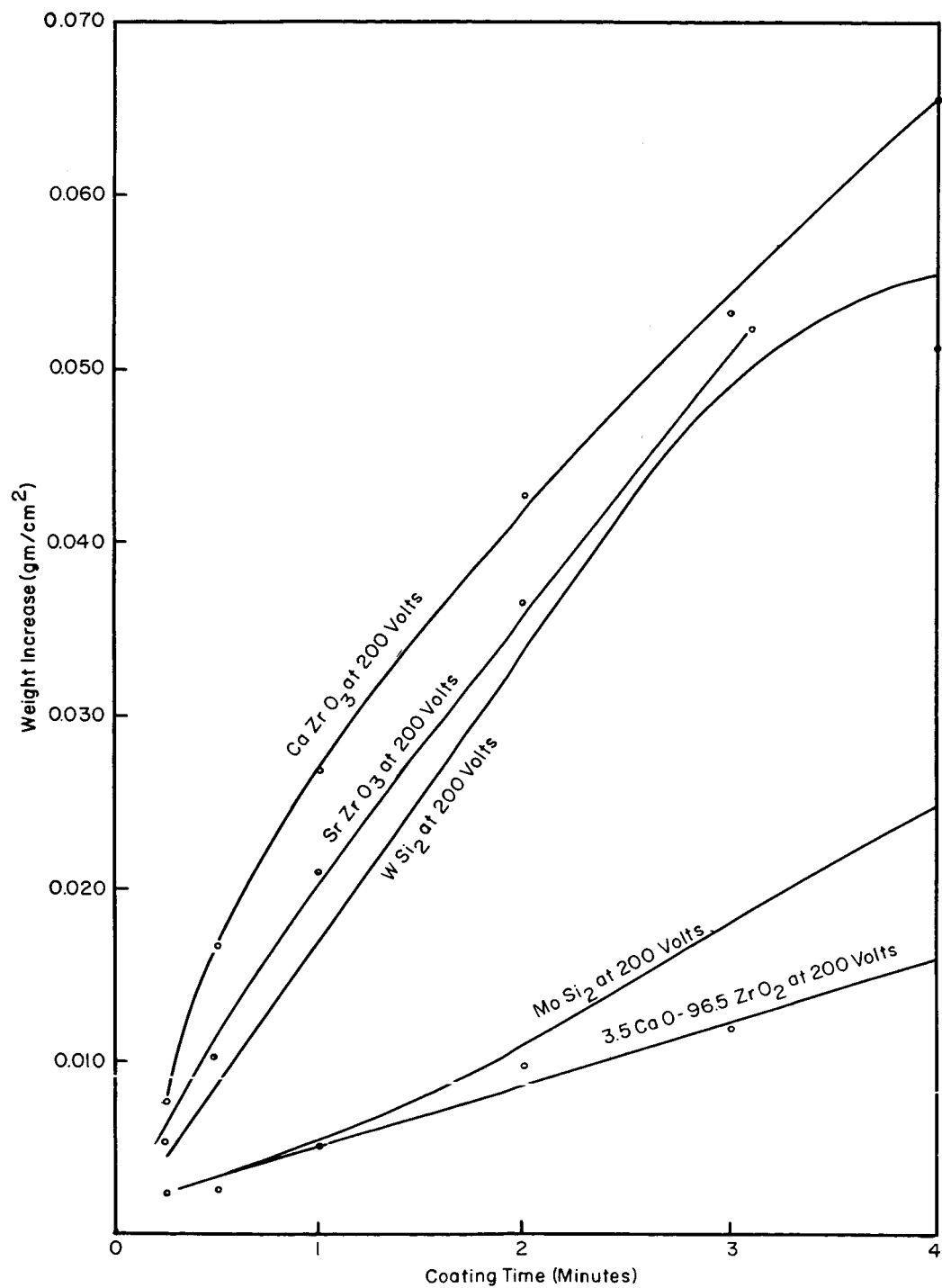


FIGURE 5  
COATING RATE OF VARIOUS 1 w/o DISPERSIONS

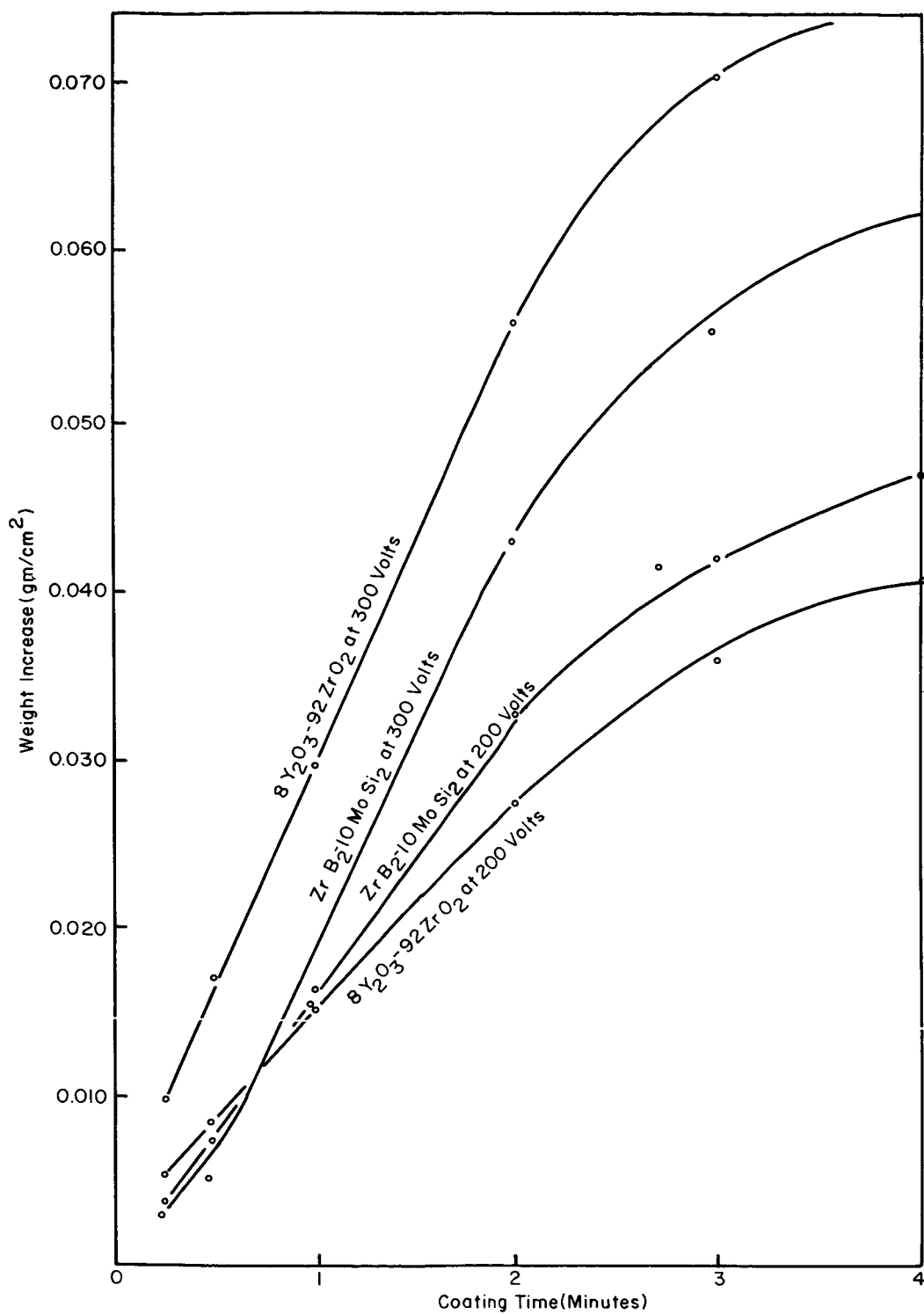


FIGURE 6  
COATING RATE OF VARIOUS 1 w/o DISPERSIONS

dispersions would be required to increase their coating rates. The curves for yttria-stabilized zirconia and  $90\text{ZrB}_2\text{-}10\text{MoSi}_2$  indicate that these dispersions may be made to coat at the same rate by operating at a potential between 200 and 300 VDC.

Experiments with gradated coatings of intermetallic compounds and oxides were performed after study of the deposition rates of the individual materials. Tungsten disilicide was selected as a model intermetallic compound and was codeposited with yttria-stabilized zirconia or with strontium zirconate to obtain gradated coatings on Ta-10W alloy panels. A number of coating trials were made to develop coating information. An example of typical coating conditions was:

Pump Motor Setting	100%
Motor Controller Setting	2 (equivalent to 5 minutes)
Voltage	200-500 VDC
Current	10ma (constant)
Delay Time (coating of $\text{WSi}_2$ )	5 minutes
Grading Time	5 minutes
Final Time (coating of oxide)	3 minutes

Under these conditions, 0.020" thick gradated green coatings were produced. This 0.020" thickness was composed of 0.008" of intermetallic, 0.006" of gradated material, and 0.006" of oxide. Isostatic pressing of the coating at 25 tsi reduced the thickness of three regions to approximately one half of the deposited values.

### 2.2.3 Particle Size Studies

The coating rate curves presented in Section 2.2.2 indicated some variation of coating rates among the dispersions of interest. These results and additional gradated coating experiments indicated that the coating rates were lower than desired. Since these rates vary considerably with the particle size distribution of the dispersed particles, a sedimentation experiment was run to check the particle size of several as-received materials.  $\text{WSi}_2$  and calcia-stabilized  $\text{ZrO}_2$  powders which passed through a 325 mesh sieve (44 microns) readily but which exhibited different coating rate curves were chosen for the study. The sedimentation experiment was similar to that reported by Skinner and Riley<sup>(1)\*</sup>. One

---

\* Superscripts refer to literature sources listed under References

hundred grams of  $\text{WSi}_2$  or  $\text{CaO}$ -stabilized  $\text{ZrO}_2$  were slurried in distilled water, and introduced into the top of a 34" high column of distilled water contained in a glass tube 3-5/8" in diameter. The powders were allowed to settle for 22 minutes, after which the suspended material was decanted and both portions were evaporated to dryness and weighed. The results were:

	<u><math>\text{WSi}_2</math></u>	<u><math>\text{CaO-Stabilized}</math> <math>\text{ZrO}_2</math></u>
Coarse Material (Approx. 16-44 microns)	57.3%	86.0%
Fine Material (Approx. 15 microns and below)	42.7%	14.0%

Thus, the experiment showed a substantial difference in the particle size distribution of these two materials.

This difference was also evident when the materials were examined under a 120 X binocular microscope. In view of these findings it appeared desirable to modify the raw powders by grinding to make their particle size distributions more similar for gradated coating applications.

Similar settling experiments were conducted on other raw powdered materials of interest including a new lot of 3.5% $\text{CaO}$ -stabilized  $\text{ZrO}_2$ . According to Stokes' Law, the 22 minute sedimentation time will remove all particles larger than 15 microns in diameter, assuming an average particle density of 6 g/cc. The pertinent equation for the time of fall ( $t$ ) of spherical particles of radius  $r$  and density  $d_1$  through a column of liquid of density  $d_2$ , height  $h$ , and viscosity  $n$ , under the gravitational acceleration  $g$  is:

$$t = 9hn/2gr^2(d_1-d_2)$$

The results of the sedimentation trials are summarized in Table 8.

TABLE 8  
SEDIMENTATION STUDIES OF SELECTED  
INTERMETALLICS AND OXIDES

<u>Material</u>	<u>History</u>	<u>% Coarse (<math>&gt;15\mu</math>)</u>
MoSi <sub>2</sub>	As received (-325 mesh)	48.70%
MoSi <sub>2</sub>	Milled for 48 hours	6.25*
3.5% CaO-stabilized ZrO <sub>2</sub>	As received (-325 mesh)	13.40
3.5% CaO-stabilized ZrO <sub>2</sub>	Milled for 6 hours	3.00
SrZrO <sub>3</sub>	As received (-325 mesh)	28.80
8%Y <sub>2</sub> O <sub>3</sub> -stabilized ZrO <sub>2</sub>	As received (-325 mesh)	32.00

\* Dried agglomerates of very fine particles

It was evident from this data that the size and distribution of particles in these raw materials varied considerably. These variations were unacceptable since the intermetallics and oxides will deposit at widely different rates. The decrease from 86% to 13% for the coarse fraction of two lots of -325 mesh calcia-stabilized zirconia obtained from the same manufacturer was particularly striking. As a result of this experiment, a ball-milling study was performed with the coarser materials to reduce their average particle size to the same range as that of the finer powders.

The results of this study showed that it was necessary to ball mill both the intermetallic and oxide materials, and then leach the powders in 50% HCl solution and dry, in order to obtain sufficiently fine powders for active sintering. The following procedure was used in the subsequent studies.

Two hundred grams of -325 mesh intermetallic or oxide material were milled in isopropanol for 48 hours in a 400 ml, chrome-manganese steel mill containing seventy, 1/2" diameter chrome-manganese steel balls. The milling speed was 150 rpm. After milling, the charge was evaporated to dryness and then leached with approximately 250 ml of a 50% HCl solution. Upon completion of leaching the material was washed several times with de-ionized water and then dried. The powder was then ready for use in electrophoretic dispersions for gradated coating experiments.

### 2.3 High Temperature (4000°F) Oxidation Test Furnace

An experimental induction-heated vertical zirconia muffle furnace (Model No. 1F-1) was purchased from the Zirconium Corporation of America, Solon, Ohio in order to conduct the oxidation tests on the various coating systems above 3500°F. A furnace of this type was recently used by Tapco for testing oxidation resistant coatings on tungsten<sup>(2)</sup>.

The furnace consists of a calcia-stabilized zirconia tube, 20 inches long with an outside diameter of 2 inches and an inside diameter of 1-1/2 inches. This muffle is surrounded by a graphite susceptor, which in turn, is encapsulated in a quartz envelope. The induction coils are positioned outside of the quartz envelope or chamber. The graphite susceptor and lampback insulation are protected from oxidation during operation by nitrogen gas flowing under a slight positive pressure through the quartz chamber. Loading and unloading of the furnace is accomplished through the use of a retractable bottom pedestal. This pedestal has a two-section shaft of calcia stabilized zirconia (1/2 inch diameter) capped with a 1/2 inch diameter zirconia disc. The disc is used as the specimen carrier. Alumina heat shields are used at the top of the zirconia muffle to operating temperatures of 3200°F and zirconia heat shields at temperatures above 3200°F. Free expansion of the zirconia muffle is allowed through the use of a bellows seal at the top portion. The recommended idling temperature for the furnace is 3000°-3200°F and its maximum operating temperature with a zirconia inner tube is 4500°F.

A gas flowmeter is provided for the output end of the furnace so that pressure drop will indicate cracked ZrO<sub>2</sub> tube or other undesirable leak, and a water line filter is used to remove foreign particles from the cooling loop. An auxiliary safety water supply system which operates to



cool the furnace by gravity feed in the event of a water pressure drop on the main supply was also installed. A photograph of the equipment is shown in Figure 7 and details of the support stand and furnace are shown in Figures 8 and 9. The initial furnace operation proved to be satisfactory. With full power of 20 kw applied to the coil, the maximum temperature reached was 2220°C (4028°F). After heat-up, a temperature of 3500°F was held with a power input of 13-15 kw.

Several small changes in the equipment were made before the oxidation tests were conducted , i. e. ,

1. the N<sub>2</sub> protective gas flowmeter was moved so that flow measurement was made on the input side of the furnace
2. the air cylinder was adjusted to obtain a smoother, more controllable motion of the pedestal
3. a smaller specimen pedestal was designed so that test specimens were more easily mounted and inserted, more easily observed during test, and easily removed from the furnace.

After a continuous run of nine days at 3200°F, the furnace was cooled for examination because the temperature could not be raised to 3500°F, regardless of power input.

An inspection of the cooled furnace showed that the graphite felt insulation had oxidized, presumably because of air leakage. The insulation was replaced and the furnace checked for gas leaks. It was then reheated satisfactorily and oxidation tests were conducted at 3500°F.

Subsequent experience with the furnace indicated that the water-cooled end seals were poorly designed and fabricated. Inadequate sealing led to inspiration of air through the thermal insulation and gradual burnup of the lampblack insulation and graphite split rings. The seals will require redesign and reinstallation if additional work is done with the furnace.

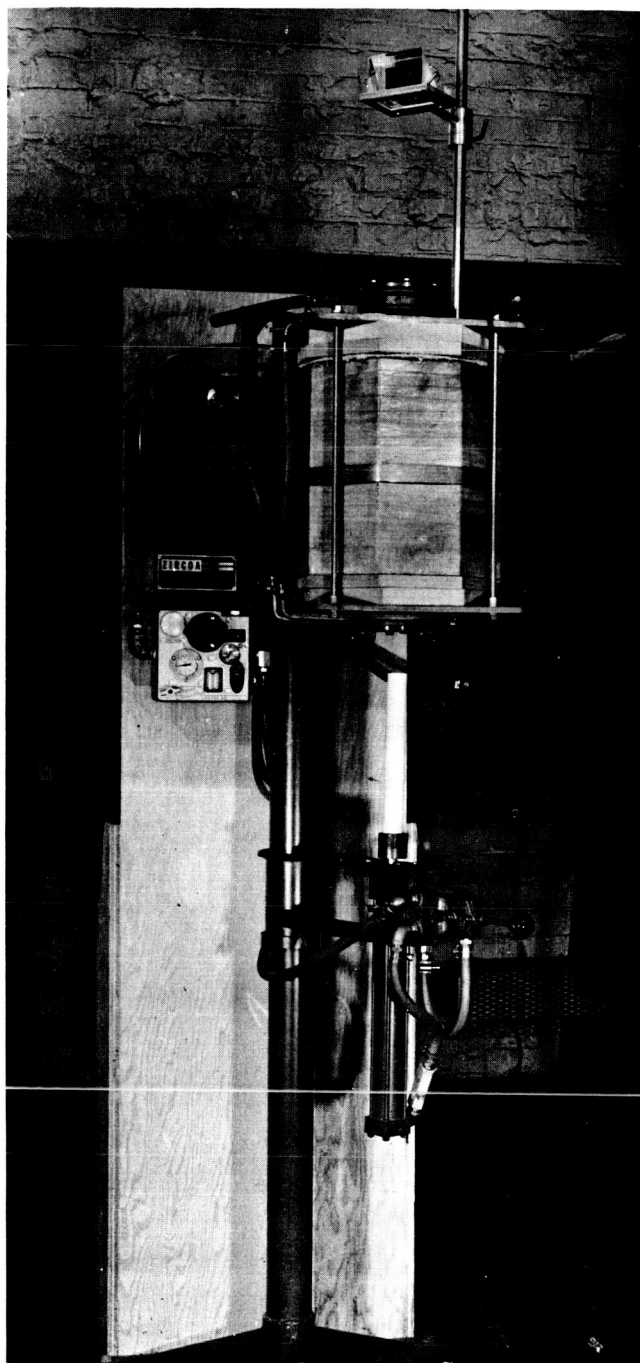


FIGURE 7  
HIGH TEMPERATURE OXIDATION TEST FURNACE

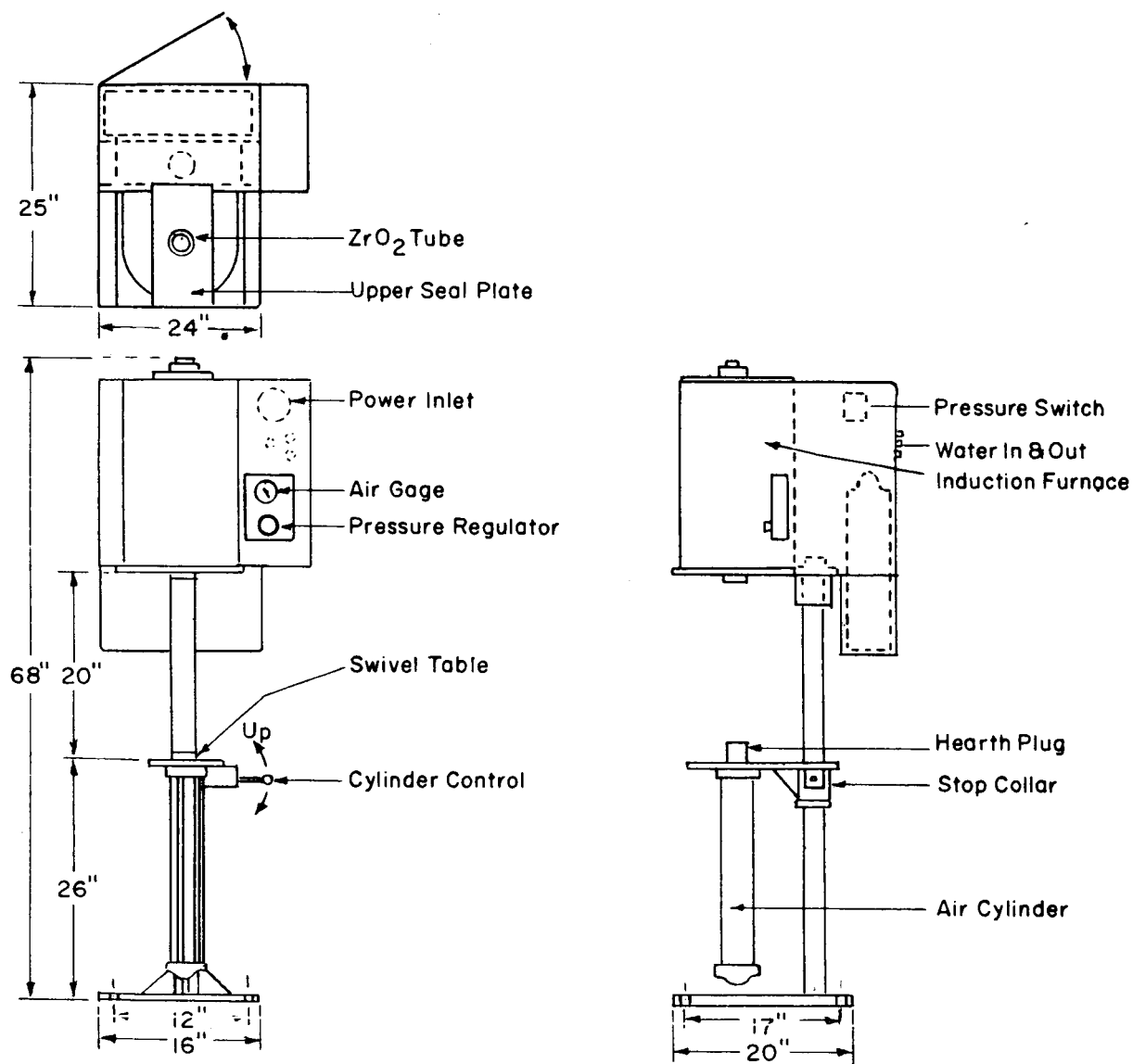


FIGURE 8  
SUPPORT STAND FOR EXPERIMENTAL ZIRCONIA  
MUFFLE INDUCTION FURNACE

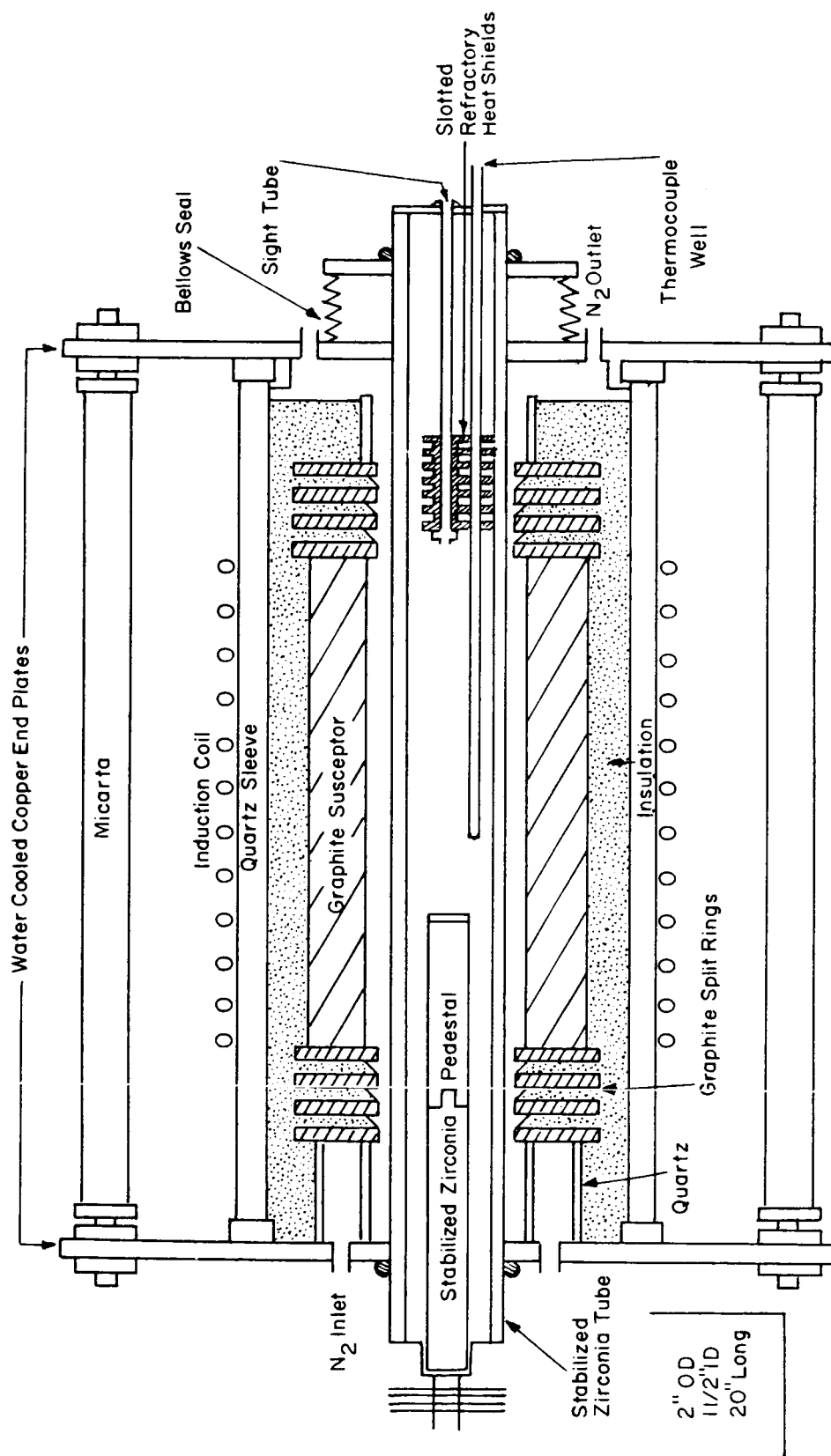


FIGURE 9  
EXPERIMENTAL INDUCTION-HEATED VERTICAL  
ZIRCONIA MUFFLE FURNACE

### 3. PRELIMINARY COATING AND SINTERING STUDIES

#### 3.1 Sintering of Pure Oxides, Pure Intermetallics and Composite Pellets

To determine the approximate temperature range required to sinter gradated coatings of the materials listed in Table 1, sintering trials were performed with the pure oxide and intermetallic compounds in the form of pressed discs. Before preparing the discs, all materials were ball-milled to 100% -325 mesh size in a chrome manganese steel mill, and the resulting powders were leached in dilute hydrochloric acid, washed, and dried. The powders were then pressed in a steel die at 20,000 psi to 0.5 in. diameter discs, and these samples were sintered under various conditions as shown in Table 9. Following sintering, the apparent density was determined by weighing in air and water, and the samples were sectioned, mounted, polished, and photographed. Photomicrographs of representative sintered intermetallic and oxide specimens are shown in Figures 10, 11, and 12.

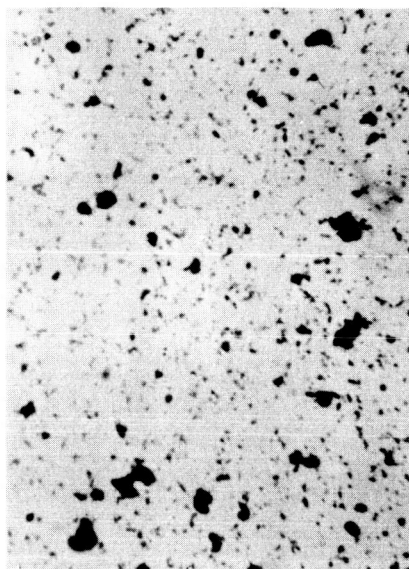
Following the work on the individual compounds, the stabilities of mixtures of 50% oxide-50% intermetallic were determined by pressing powder blends and sintering the composite discs for various intervals of time at temperatures to 1700°C. The results are shown in Table 10, and photomicrographs of typical sintered composites are shown in Figures 13 and 14.

Based upon these studies,  $Y_2O_3$ -stabilized  $ZrO_2$ ,  $CaZrO_3$  or  $SrZrO_3$  in combination with any of the intermetallic compounds looked promising for future study as gradated coatings. Additional screening of these composites was made by checking their oxidation resistance in torch tests at temperatures between 3100° and 4500°F.

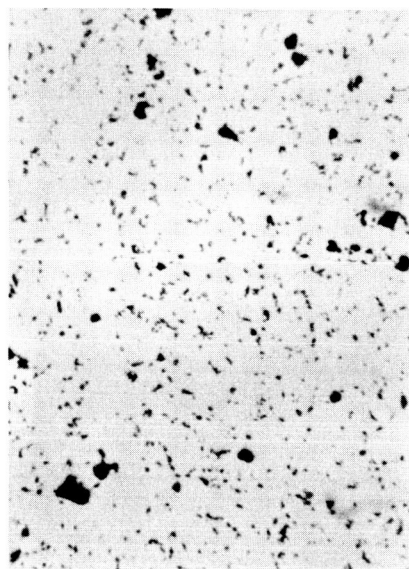
#### 3.2 Coating and Bonding of Intermetallic Compounds

##### 3.2.1 Adherence and Eutectic Problem

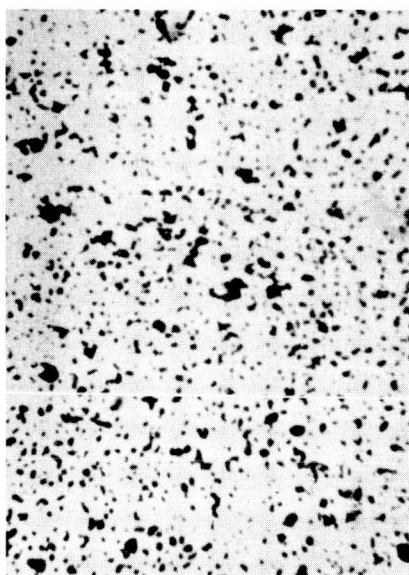
Preliminary studies to determine optimum sintering conditions for the intermetallic coatings indicated that the adherence of these materials to the Ta-10W substrate was a major problem. A series of coating materials were deposited on Ta-10W panels, and these samples were heated to 1750-1800°C in argon for one hour. The results of this test



TaAl<sub>3</sub> 1 hr., 1400°C, Argon



Ta<sub>2</sub>Be<sub>17</sub> 2.5hrs, 1400°C, Argon

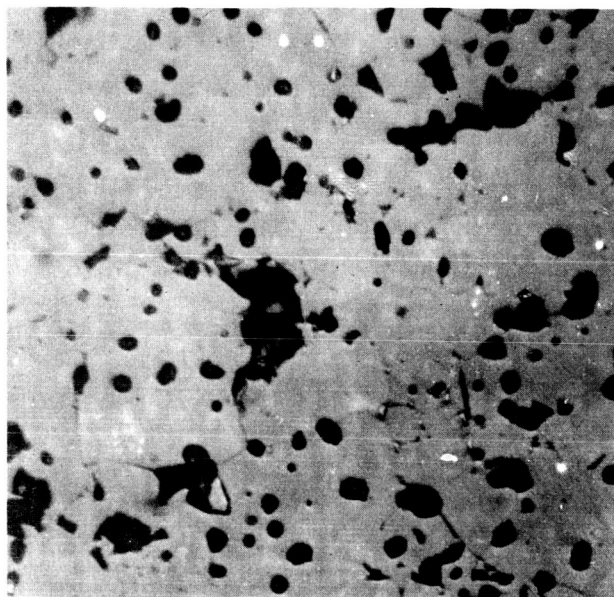


TaSi<sub>2</sub> 1hr., 1400°C, Argon



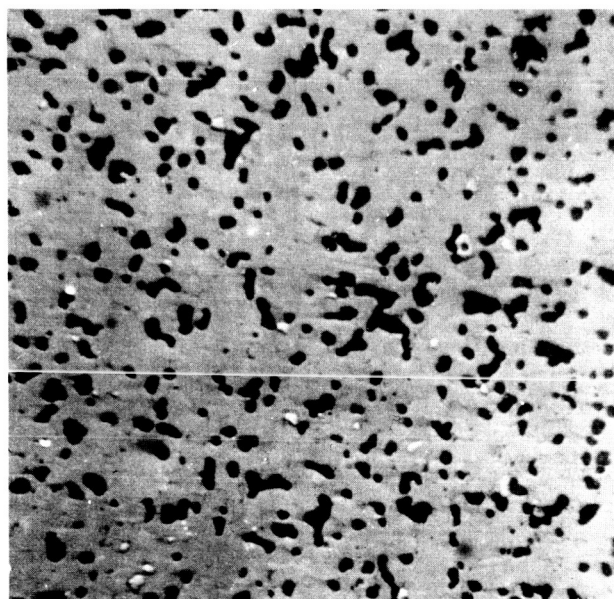
90 Zr B<sub>2</sub>-10 Mo Si<sub>2</sub>-1hr., 1400°C, Argon

FIGURE 10  
PHOTOMICROGRAPHS OF SINTERED  
INTERMETALLIC COMPOUNDS  
(400 × Magnification, Unetched)



$\text{CaZrO}_3$

540x  
Unetched



$\text{SrZrO}_3$

540x  
Unetched

FIGURE 11  
PHOTOMICROGRAPHS OF  
SINTERED  $\text{CaZrO}_3$  AND  $\text{SrZrO}_3$   
(Sintering Conditions - 45 min., 1700°C in Argon)



5 hrs -1725°C -Argon

400x , Unetched

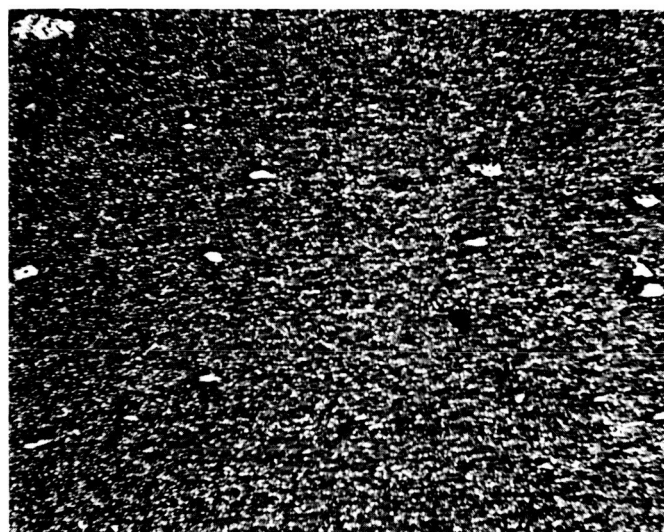


10 hrs -1725°C -Argon

800x , Unetched

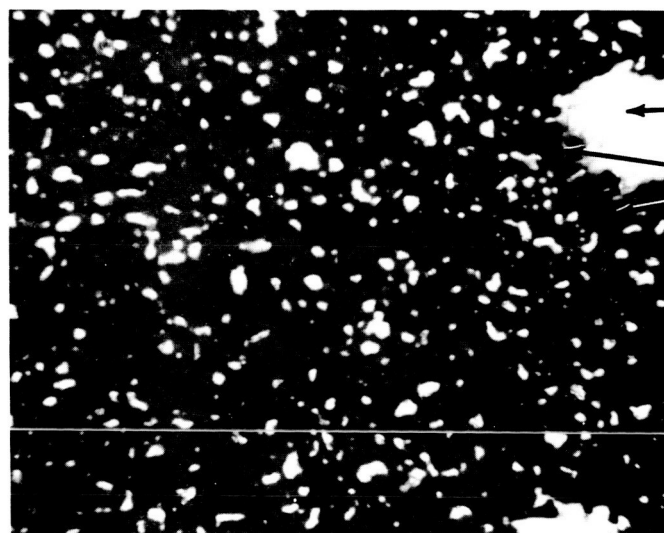
FIGURE 12  
 PHOTOMICROGRAPHS OF  
 SINTERED 8% Y<sub>2</sub>O<sub>3</sub>-STABILIZED ZrO<sub>2</sub>





$\text{SrZrO}_3\text{-TaSi}_2$   
Density = 80% Theory

80x  
Unetched



$50\text{SrZrO}_3\text{-}50(90\text{ZrB}_2\text{-}10\text{MoSi}_2)$   
Density = 75% Theory

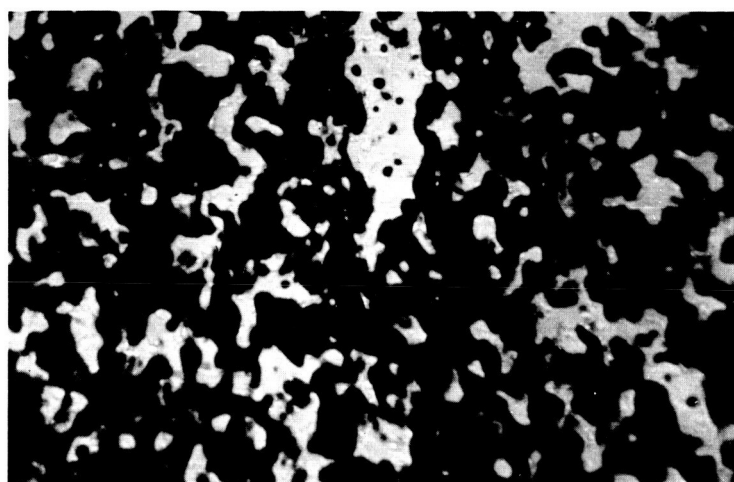
350x  
Unetched

←  $90\text{ZrB}_2\text{-}10\text{MoSi}_2$   
Void  
←  $\text{SrZrO}_3$

FIGURE 13

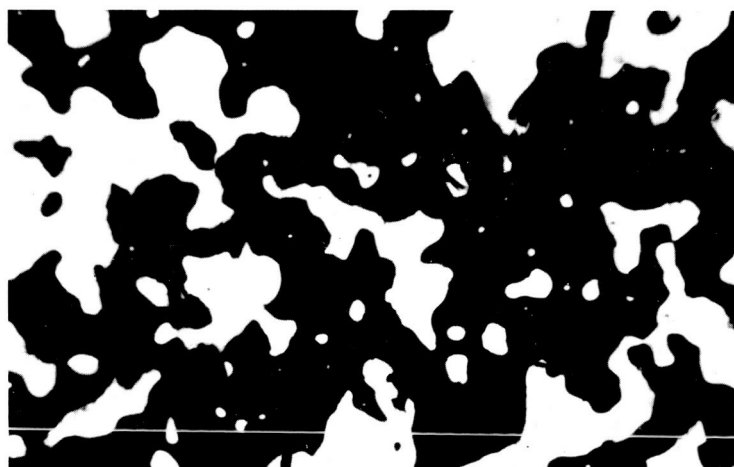
PHOTOMICROGRAPHS OF  $50\text{SrZrO}_3\text{-}50\text{TaSi}_2$   
AND  $50\text{SrZrO}_3\text{-}50(90\text{ZrB}_2\text{-}10\text{MoSi}_2)$

(Sintered at  $1700^\circ\text{C}$  for 30 Minutes in Argon)



50(8Y<sub>2</sub>O<sub>3</sub>-92ZrO<sub>2</sub>)-50MoSi<sub>2</sub>

400x



50(8Y<sub>2</sub>O<sub>3</sub>-92ZrO<sub>2</sub>)-50(90ZrB<sub>2</sub>-10MoSi<sub>2</sub>)

400x

FIGURE 14

PHOTOMICROGRAPHS AT 400 × MAGNIFICATION OF  
8% Y<sub>2</sub>O<sub>3</sub> - STABILIZED ZrO<sub>2</sub> COMPOSITES

(Sintered 3.5 Hrs. at 1725°C in Argon)

TABLE 9  
SINTERING TRIALS OF OXIDES AND INTERMETALLIC COMPOUNDS

	<u>Sintering Conditions*</u>	<u>Apparent Density</u>	
		<u>g/cc</u>	<u>% Theoretical</u>
90ZrB <sub>2</sub> -10MoSi <sub>2</sub>	a	5.82	95
TaSi <sub>2</sub>	a	8.30	91
Ta <sub>2</sub> Be <sub>17</sub>	a	(Powdery, did not sinter)	
	e	4.7	93
TaAl <sub>3</sub>	a	6.18	89
Al <sub>2</sub> O <sub>3</sub>	c	3.50	88
SrZrO <sub>3</sub>	a	4.44	81
	b	4.45	81
	c	4.90	89
CaZrO <sub>3</sub>	a	3.48	73
	b	3.89	81
	c	4.12	86
8Y <sub>2</sub> O <sub>3</sub> -92ZrO <sub>2</sub>	a	4.29	76
	b	4.44	78
	d	5.05	89
	f	4.80	85
	g	4.93	87
3.5CaO-96.5ZrO <sub>2</sub>	b	3.99	71
	c	4.18	74
	f	4.66	83.5
	g	5.05	89

\*  
Conditions

- a) 60 min., 1400°C in Argon
- b) Same as (a), then 15 min., 1700°C in Argon
- c) 45 min. 1700°C in Argon
- d) 45 min., 1900°C, 10<sup>-6</sup> Torr
- e) 150 min. 1400°C in Argon
- f) 5 hrs. 1725°C in Argon
- g) 10 hrs. 1725°C in Argon

TABLE 10

DENSITY OF SINTERED BLENDS OF  
50% INTERMETALLIC COMPOUND - 50% REFRACTORY OXIDE  
(Sintering Conditions: 1/2 or 3-1/2 Hrs. at 1700°C in Argon)

	<u>Intermetallic Compound</u>					
	<u>TaAl<sub>3</sub></u>	<u>Ta<sub>2</sub>Be<sub>17</sub></u>	<u>TaSi<sub>2</sub></u>	<u>90ZrB<sub>2</sub>-10MoSi<sub>2</sub></u>	<u>MoSi<sub>2</sub></u>	
<u>OXIDE</u>						
3.5 CaO-96.5ZrO <sub>2</sub>	6.28 4.60 73	5.35 1.7 30	7.37 6.10 83*	5.88 5.50 94*	5.94 5.90 99*	Calc. Density App. Density % Theory
8Y2O <sub>3</sub> -92ZrO <sub>2</sub>	6.29 4.73 75	5.36 --- ---	7.38 7.37 99*	5.89 5.88 99*	5.95 5.64 95*	Calc. Density App. Density % Theory
CaZrO <sub>3</sub>	5.85 4.56 78	4.92 3.25 66	6.94 4.93 71	5.45 4.58 84	5.51 --- ---	Calc. Density App. Density % Theory
SrZrO <sub>3</sub>	6.20 5.15 67	5.26 2.49 47	7.29 5.84 80	5.80 4.35 75	5.86 4.60 78	Calc. Density App. Density % Theory
Al <sub>2</sub> O <sub>3</sub>	5.44 1.79 33	4.50 --- ---	6.53 3.80 58	5.04 2.87 57	5.10 3.16 62	Calc. Density App. Density % Theory

\* Sintered 3 1/2 hours at 1700°C

are shown in Figure 15. Tantalum silicide and tungsten silicide plus 10%ZrB<sub>2</sub>-10MoSi<sub>2</sub> reacted with the substrate to form a molten phase. The remaining materials; pure ZrB<sub>2</sub>-10MoSi<sub>2</sub> plus 10% MoSi<sub>2</sub> or tantalum, MoSi<sub>2</sub>, and -10 micron tantalum each sintered, but none adhered to the substrate.

In many cases the Ta-10W substrate became embrittled during sintering. Two possible sources of embrittlement which were considered were diffusion of one or more of the components of the intermetallic coating into the substrate and contamination of the substrate by reaction with impurities in the furnace atmosphere.

In an effort to improve the sinterability and adherence of the intermetallic compounds, the ZrB<sub>2</sub>-10MoSi<sub>2</sub>, WSi<sub>2</sub>, TaSi<sub>2</sub>, and MoSi<sub>2</sub> were screened through -325 mesh, and the fines used for coating a set of Ta-10W panels. The panels were then isostatically pressed at 25 tsi and sintered in argon for one to two hours at 1700°-1800°C. The results are summarized in Table 11. To check the effects of heat treatment on the ductility of the substrate, an uncoated panel was heated at 1700°-1750°C in argon for one hour and hardness measurements were made of this specimen and of an uncoated, unheated panel. After heat-treatment, the substrate microhardness increased from 340 kg/mm<sup>2</sup> to 470 kg/mm<sup>2</sup>, however, the sample retained its bright appearance and remained ductile. Other hardness measurements of the coated samples are listed in Table 12. Substrates coated with ZrB<sub>2</sub>-10MoSi<sub>2</sub> were invariably embrittled after heat-treatment and diffusion of some component of the coating into the substrate took place. The silicide coatings, in general, had little effect upon the substrate ductility as evidenced by the microhardness measurements of Table 12.

### 3.2.2 Study of Metallic Binders for ZrB<sub>2</sub> and MoSi<sub>2</sub> Coatings

In initial experiments on the effect of metallic binders, ten weight percent of -325 mesh chromium, nickel, and tantalum powders were added to dispersions of 90ZrB<sub>2</sub>-10MoSi<sub>2</sub> and MoSi<sub>2</sub>, coatings were deposited on Ta-10W panels, and the coatings were pressed at 20 tsi and sintered for one hour in argon at 1700°-1750°C. The results, summarized in Table 13, indicate that both chromium and nickel binders caused severe embrittlement of the substrate and that nickel was ineffective in improving adherence of the coatings to the substrate. The tantalum binder had no effect upon either the ductility of the substrate or the adherence of the coating.

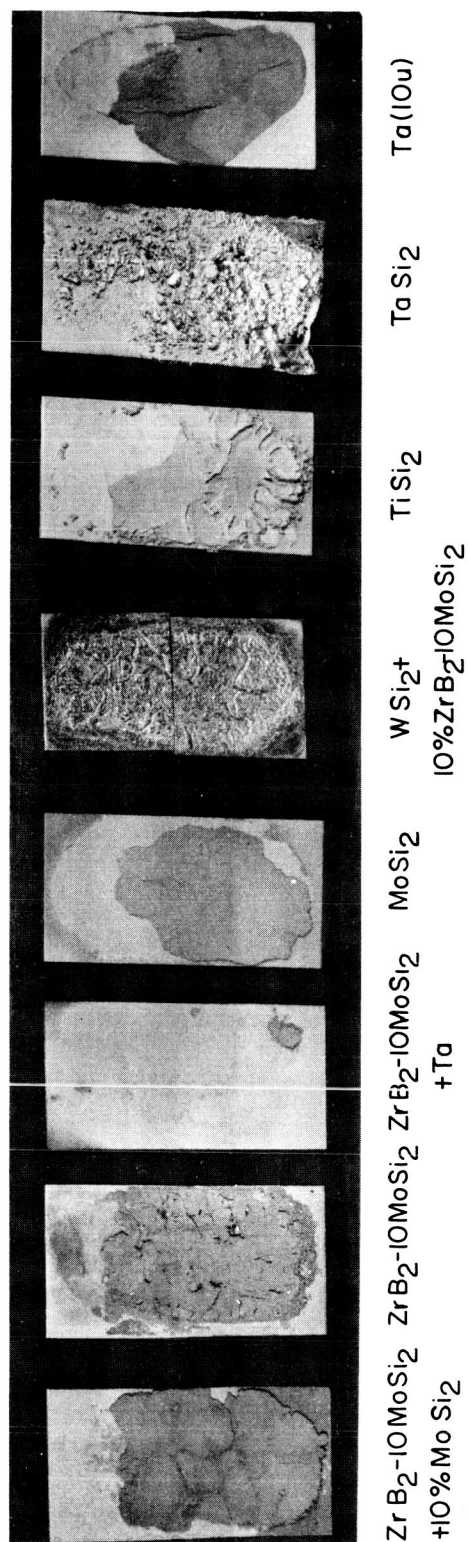


FIGURE 15  
 REACTION OF INTERMETALLIC COMPOUNDS WITH  
 Ta-10W AT 1750°C - 1800°C IN ARGON

TABLE 11  
SINTERING EXPERIMENTS-INTERMETALLIC COMPOUNDS ON Ta-10W

<u>Intermetallic Coating</u>	<u>Sintering Time and Temp. (<math>^{\circ}</math>C)</u>	<u>Results</u>
ZrB <sub>2</sub> -10 MoSi <sub>2</sub>	1700-1750, 2 hrs	Coating pressed 25 tsi, good sintering characteristics deep diffusion into substrate, good adherence.
ZrB <sub>2</sub> -10 MoSi <sub>2</sub>	1700-1750, 1 hr	Coating not pressed, sintered well, poor bonding to substrate, narrow diffusion zone.
ZrB <sub>2</sub> -10 MoSi <sub>2</sub>	temp held steady @ 1800 $^{\circ}$ C - 1 hr	Coating pressed 25 tsi, good sintered coating, good adherence, deep diffusion.
WSi <sub>2</sub>	1750-1775 - 1 hr	Coating unpressed, coating material reacted with substrate.
WSi <sub>2</sub>	1700-1750 - 1 hr	Coating pressed 25 tsi, coating sintered, slight oxidation, good adherence to substrate.
TaSi <sub>2</sub>	1700-1750 -2 hrs	Coating pressed 25 tsi, sintered well, slight diffusion, good adherence.
MoSi <sub>2</sub>	1650-1700, 1 hr	Coating material melted, very slight reaction and bonding to substrate.
ZrB <sub>2</sub> -10 MoSi <sub>2</sub> +10%Cr	1700-1750 $^{\circ}$ C, 1 hr	Pressed coating 25 tsi, reacted with substrate, substrate very brittle, coating spalled on cooling.

TABLE 12  
KNOOP HARDNESS MEASUREMENTS FOR  
INTERMETALLIC COATINGS ON Ta-10W SUBSTRATE

<u>Coating Composition</u>	<u>Sintering Conditions</u>	<u>Knoop Hardness Numbers Using a 50 Gram Load</u>		
		<u>Coating</u>	<u>Interface</u>	<u>Substrate</u>
ZrB <sub>2</sub> -10 MoSi <sub>2</sub>	1700°-1750°C, 2 hrs	3630	791-695	468-445
TaSi <sub>2</sub>	1700°-1750°C, 2hrs	549	4941-1235	385-367
Ta-10W	as received	-	-	361-322
Ta-10W	1700°-1750°C, 1 hr	-	-	473-468
WSi <sub>2</sub>	1700°-1750°C, 1 hr	1971	581	361-322
MoSi <sub>2</sub>	1650°-1700°C, 1 hr	-	-	445
ZrB <sub>2</sub> -10MoSi <sub>2</sub> +10%Cr	1700°-1750°C, 1 hr	-	-	520-473



TABLE 13  
EFFECT OF METALLIC BINDERS ON DUCTILITY OF  
Ta-10W SUBSTRATE AND ADHERENCE OF COATINGS

Intermetallic Compound	Cr	Ni	Ta
ZrB <sub>2</sub> -10 MoSi <sub>2</sub>	Sintered well, good adherence reacted severely with substrate rendering it highly embrittled	Embrittled substrate, did not enhance bonding	sintered well, No adherence to the substrate-substrate ductile.
MoSi <sub>2</sub>	Melted and reacted with substrate causing severe embrittlement	Sintered well, did not promote better bonding to the substrate. Substrate embrittled.	Coating sintered, no adherence to the substrate. Substrate ductile.

### 3.2.3 Study of Diffusion Barriers for the ZrB<sub>2</sub>-10MoSi<sub>2</sub> Coating System

In an effort to overcome the embrittlement of the Ta-10W substrate caused by interaction with the ZrB<sub>2</sub>-10MoSi<sub>2</sub> coating system, a study was made of the effect of interposing molybdenum and tungsten diffusion barriers between the coating and the substrate.

To apply the molybdenum barrier, the substrate was grit-blasted, chemically cleaned in an etchant containing 1HF:1HNO<sub>3</sub>:3 lactic acid by volume, and washed in distilled water. Molybdenum metal was then electro-phoretically deposited and the coating was isostatically pressed at 20 tsi and heat treated at 1400°C for 2 hours in argon. The resultant coating, as shown in Figure 16 was dense and well-bonded to the substrate, and no evidence was observed of contamination at the coating-substrate boundary.

The hardness of the substrate after Mo coating was found to be 322 Knoop (50 gm load) as compared to KHN 235 (50 gm load) for an untreated Ta-10W alloy. Although the coated Ta-10W alloy was somewhat harder, it still exhibited good ductility. Simultaneous efforts in another program at Vitro produced W coatings on sandblasted and chemically cleaned Ta-10W substrates<sup>(3)</sup>. These coatings were adherent, the coating-substrate interface was clean and only slight embrittlement of substrate occurred during processing. Since these results were similar to those obtained in this program with molybdenum on sandblasted and chemically cleaned Ta-10W, tungsten, as well as molybdenum, was considered for use as a diffusion barrier. A recent paper on this subject<sup>(4)</sup> indicated that tungsten and rhenium are the best of the available refractory metals (m.p. above 1700°C) for minimizing diffusion of tantalum. A summary of the data obtained in this study is shown in Table 14.

Coatings of ZrB<sub>2</sub>-10MoSi<sub>2</sub> were then deposited over the molybdenum and tungsten barriers on Ta-10W and the intermetallic coating was sintered at 1650°C for 2 hours in argon. The adherence of the coating to the tungsten barrier was poor, and the coating split and peeled from the substrate upon cooling from the sintering temperature. Microhardness measurements of the ZrB<sub>2</sub>-10MoSi<sub>2</sub> coating on the molybdenum barrier indicated some reduction in hardening of the substrate, however, embrittlement still occurred after sintering. These coating systems were therefore abandoned in favor of WSi<sub>2</sub>-base coating systems which did not degrade the mechanical properties of the substrate, and which evidenced good adherence.

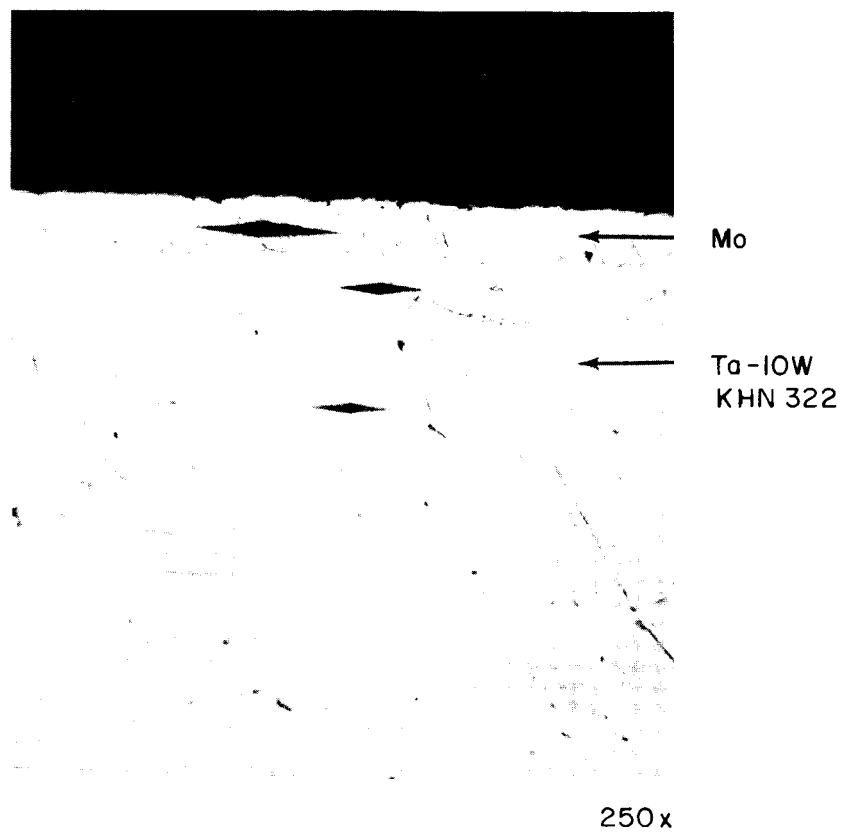


FIGURE 16

Mo COATING ON CHEMICALLY CLEANED Ta-10W  
FIRED IN ARGON AT 1400°C FOR 2 HOURS

TABLE 14

## EVALUATION OF DIFFUSION BARRIERS FOR TANTALUM

(Diffusion-annealed 4 hrs. at 1700°C or 3 hrs. at 1800°C in Argon)

<u>Couple</u>	<u>Total Diffusion Zone Thickness(<math>\mu</math>)</u>	<u>Porosity</u>	<u>Predominant Diffusion Direction</u>	<u>Diffusion Zone Hardness (KHN)</u>	
				<u>Increment</u>	<u>Maximum</u>
Ta-W (1800°)	20	Some	Into W	450	770
Ta-Re	< 50	None	Into Re	200	470
Ta-Re (1800°)	15	Little	Into Re	265	300
Ta-Ru	30	None	Equal	600	890
Ta-Ru	45	None	Into Ta	920	1050
Ta-Ir	40	None	Into Ta	990	1350
Ta-Ir (1800°)	40	Some	Into Ta	1175	1480
Ta-Hf	630	None	Into Ta	410	470
Ta-V*	125	Some	Into Ta	415	600
Ta-Cr*	360	Some	Into Ta	200	820
Ta-Pt*	40 - 100	None	Unknown	880 - 1030	1250

\* 1 Hour annealing at 1700°C

### 3.3 Tungsten Disilicide as a Base Coating Material

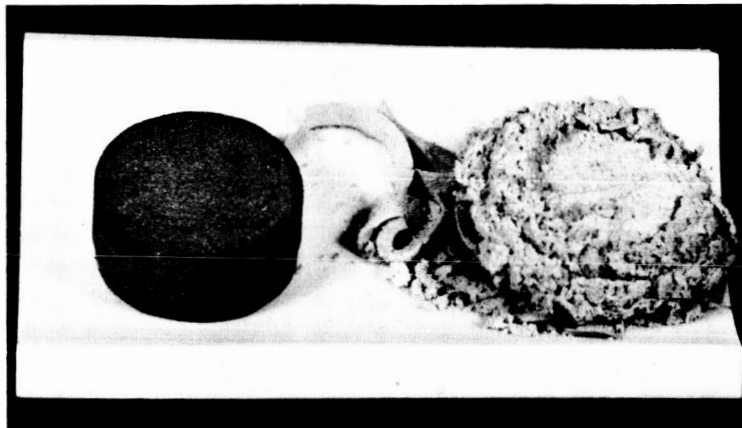
Tungsten disilicide was investigated as a base coating on Ta-10W for possible use in bonding to a graded  $\text{WSi}_2$ -refractory oxide coating. The importance of maintaining high purity in the intermetallic compounds used for coatings was demonstrated when  $\text{WSi}_2$  powders from two different commercial sources were compared in sintering and oxidation tests. Pellets of the two materials were pressed at 1000 psi and sintered in argon at  $1400^\circ\text{C}$  for 1 hour. The two types of material were then exposed side-by-side in an oxidation test. The results are shown in Figure 17. Specimen No. 7-1 shows material from Source "A" which oxidized rapidly at  $1100^\circ\text{F}$ , apparently because of the free metal present. The Source "B"  $\text{WSi}_2$  material, however, was quite stable, as shown in Specimen No. 7-2 in the photograph. Source "B" pellets were heated to  $3902^\circ\text{F}$  without signs of deterioration. These pellets are shown on the bottom half of Figure 17.

In the preliminary coating work,  $\text{WSi}_2$  from Source "A" was used exclusively as the Source "B" material was not obtained until later in the program. Coatings of this material were applied electrophoretically to sandblasted and chemically cleaned Ta-10W substrates. The coatings were densified at 30 tsi, and heat treated in argon at  $1400^\circ\text{C}$  for one hour. The resultant coatings appeared quite dense and adherent to the substrates.

An alternate heat-treating procedure, designed to eliminate any free tungsten in the tungsten silicide powder, and to improve the density of the coating consisted of embedding the coated specimen in silicon metal powder and heating at  $1350^\circ\text{C}$  for a minimum of two hours in an argon atmosphere. Good bonding to the substrate was evident and the heat treatment did not appreciably affect the ductility of the substrate.

In a static oxidation test at  $3000^\circ\text{F}$ , the coating resisted penetration by oxygen for 30 minutes even though it was only one mil thick.

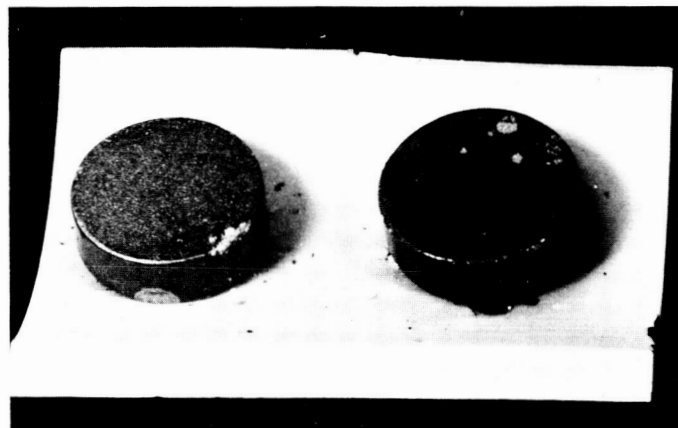
In separate studies it was found that an optimum coating is produced by sintering the  $\text{WSi}_2$  for 2 hours at  $1600^\circ\text{C}$  in argon, followed by 16 hours siliconization at  $1350^\circ\text{C}$  and a pressure less than 0.1 torr. A comparison of a 1-hour and 16-hour-siliconized  $\text{WSi}_2$  coating is shown in Figure 18.



No. 7-2

No. 7-1

1100°F (Approx.)- Short Time

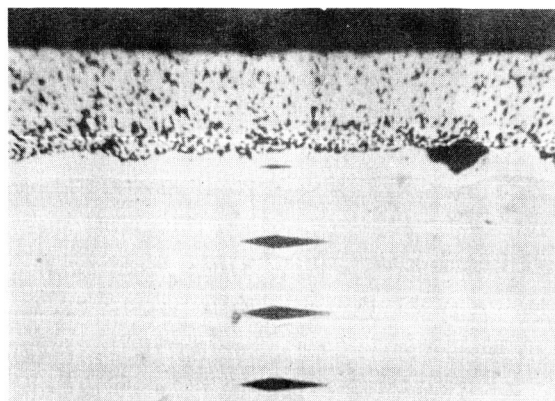


No. 7-3

3092°F - 1 1/2 Hours

FIGURE 17

WSi<sub>2</sub> PELLETS AFTER STATIC OXIDATION TESTS



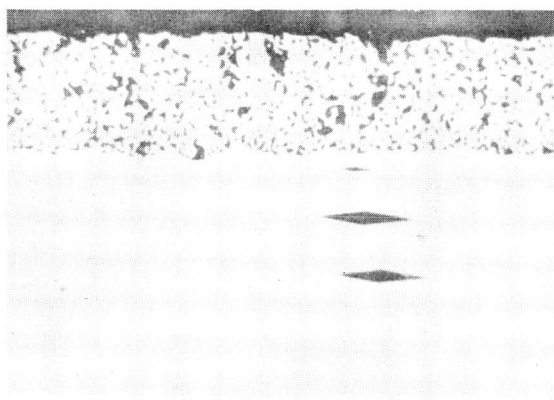
W Si<sub>2</sub>

Diffusion Zone 1140 kg/mm<sup>2</sup>

Ta-10W 245 kg/mm<sup>2</sup>

Siliconized 1 hr  
1350°C in Argon

250x, Unetched



W Si<sub>2</sub>

Diffusion Zone 1470 kg/mm<sup>2</sup>

Ta-10W, 320 kg/mm<sup>2</sup>

16 hr Siliconization  
1300°C, < 0.1 Torr

250x, Unetched

FIGURE 18

EFFECT OF SILICONIZATION PROCEDURE ON  
WSi<sub>2</sub> COATING ON Ta-10W, SINTERED AT 1600°C

The preliminary test results with this material were very promising and it was anticipated that a  $\text{WSi}_2$  coating, prepared in the manner described, would serve as an excellent base for  $\text{WSi}_2$ -oxide graded coatings on Ta-10W alloy substrates.

The higher purity  $\text{WSi}_2$  obtained from Source "B" was tested separately, after coating, sintering and vacuum siliconizing, as an oxidation resistant coating on Ta-10W at temperatures of  $3000^\circ\text{F}$  and  $3200^\circ\text{F}$  in static air. Individual specimens developed a smooth, self-healing, viscous  $\text{SiO}_2$  glass surface during the tests. Protective life for five different specimens at  $3200^\circ\text{F}$  varied from 3 to 5-1/2 hours. The specimens were removed from the furnace when evidence of edge or corner failure appeared. Because of these promising results the Source "B"  $\text{WSi}_2$  was used in the subsequent preparation of graded coatings with this intermetallic compound.

#### 3.4 Sintering Studies of Oxides

Studies were undertaken to increase the density and/or imperviousness of the refractory oxide component of the graded coating system by the addition of a second phase (fluxing component). The purpose of this material was to provide a liquid phase at temperatures lower than the melting temperature of the primary refractory oxide. This liquid phase acts as a sintering aid by promoting material transport, leading to increased densification rates and higher ultimate densities.

Various investigators have studied the effect of metal and oxide additions to zirconia. Ruh, et al<sup>(5)</sup> note the effect of liquid phase titanium in promoting the sintering of zirconia. In other work, Ruh and Garrett<sup>(6)</sup> demonstrated the increased sintering rate of zirconia by additions of chromium in quantities above the solubility limit, i. e., over 1%. This is another example of the beneficial effect of liquid phase formation during sintering.

Additions other than metals were thought to prove more useful for present purposes; for example any one of a number of oxides which combine with zirconia to form eutectics which melt at temperatures below the melting point of zirconia itself. A number of potentially applicable liquidus curves<sup>(7)</sup> for zirconia and other oxides are shown in Figures 19 and 20.



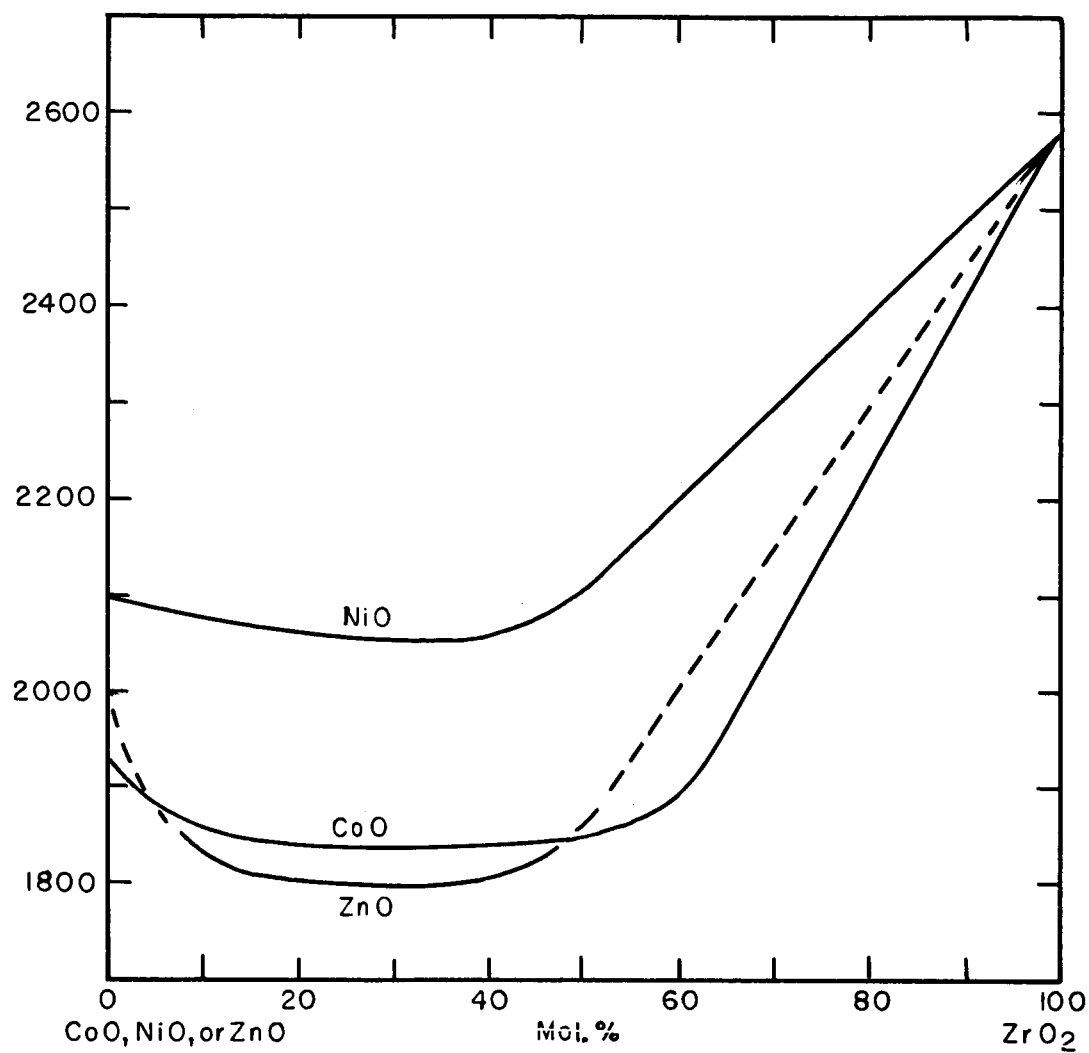


FIGURE 19  
LIQUIDUS CURVES OF SYSTEMS  
CoO-ZrO<sub>2</sub>, NiO-ZrO<sub>2</sub>, AND ZnO-ZrO<sub>2</sub>

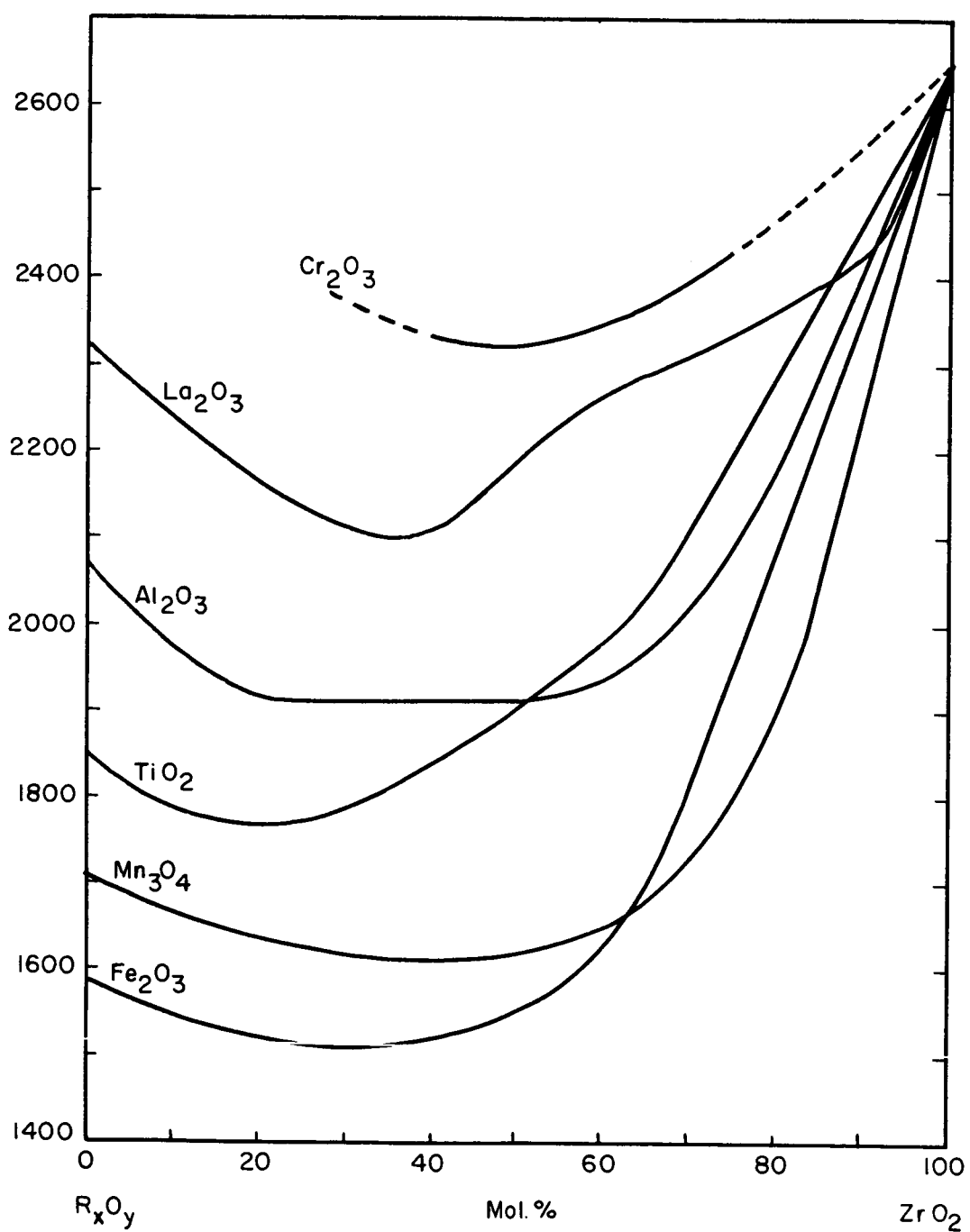


FIGURE 20  
LIQUIDUS CURVES OF SYSTEMS  $Al_2O_3$ - $ZrO_2$ ,  $Cr_2O_3$ - $ZrO_2$ ,  
 $Fe_2O_3$ - $ZrO_2$ ,  $La_2O_3$ - $ZrO_2$ ,  $Mn_3O_4$ - $ZrO_2$ , AND  $TiO_2$ - $ZrO_2$

One experiment was performed in which a pellet composed of 90 w/o (3.5%CaO-ZrO<sub>2</sub>) and 10 w/o TiO<sub>2</sub> was treated at 1700°C for two hours in an argon atmosphere. This pellet was fused and hard and an extensive, even excessive, amount of liquid phase was present during sintering to aid the densification. Considerable effort was devoted to the preparation, sintering, and study of 3.5% CaO-stabilized ZrO<sub>2</sub> samples to which various potential fluxing materials were added.

Ten gram batches of each composition were weighed, isopropyl alcohol was added, and the sample was mixed thoroughly in a mortar while the alcohol evaporated. The mixed material was then dry-pressed into 1/2" diameter x 1/8" thick pellets. These pellet specimens were sintered in argon at 1700°C for two hours.

The results of these experiments are listed in Table 15. The materials which appeared to have the greatest effect in promoting the densification of CaO-stabilized ZrO<sub>2</sub> at 1700°C were TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>. Two zirconia compositions; one containing 2 w/o TiO<sub>2</sub> and another containing 5 w/o Al<sub>2</sub>O<sub>3</sub>, were therefore investigated for use as the oxide component in gradated coatings applied by electrophoretic deposition.

#### 4. GRADATED COATINGS - PREPARATION AND TESTING

##### 4.1 MoSi<sub>2</sub>-Refractory Oxide Systems

Preliminary experiments were conducted with the MoSi<sub>2</sub> system in order to establish optimum conditions for obtaining good adherence to the Ta-10W substrate. Table 16 summarizes the significant experiments which were performed. In all cases the Ta-10W substrates were prepared by sand-blasting and etching for 5 minutes in a Lactic Acid-HNO<sub>3</sub>-HF mixture. The following variables were investigated:

1. Particle size of the solids in dispersion:

A comparison was made between coarse MoSi<sub>2</sub> particles (less than 15 microns obtained by settling), and fine MoSi<sub>2</sub> particles (less than 5 microns) obtained by ball-milling for 40 hours.

TABLE 15  
RESULTS OF SINTERING FLUXED  $\text{ZrO}_2$   
AT  $1700^\circ\text{C}$  FOR 2 HOURS IN ARGON

<u>Composition</u>			<u>Appearance</u>
$\text{ZrO}_2$	99% - $\text{TiO}_2$	1%	White, porous
	98%	2%	Light brown, surface impervious, glassy
	95%	5%	Dark brown, impervious, glassy
	90%	10%	Dark brown, impervious, glassy
$\text{ZrO}_2$	99% - $\text{Co}_2\text{O}_3$	1%	Pale green, porous
	98%	2%	Pale green, porous
	95%	5%	Dark gray, impervious
	90%	10%	Dark gray, impervious
$\text{ZrO}_2$	99% - Cr	1%	Gray, porous
	98%	2%	Gray, porous
	95%	5%	Gray, porous
	90%	10%	Gray, porous
$\text{ZrO}_2$	99% - $\text{Al}_2\text{O}_3$	1%	White, porous
	98%	2%	White, porous
	95%	5%	White, impervious
	90%	10%	White, impervious
$\text{ZrO}_2$	100%		White, impervious

TABLE 16  
SINTERING TRIALS OF MoSi<sub>2</sub>-OXIDE COATINGS ON Ta-10W

	<u>Intermetallic Coating</u>	<u>Oxide Coating</u>	<u>Pressing Pressure</u>	<u>Sintering Conditions</u>	<u>Results</u>
1	MoSi <sub>2</sub> < 15 microns	-	20 tsi	1400°C 1 hr.	Non-adherent soft coating
2	MoSi <sub>2</sub> < 5 microns	-	20 tsi	1400°C 1 hr.	Adherent soft coating
3	MoSi <sub>2</sub> < 15 microns	-	30 tsi	1500°C 2 hrs.	Non-adherent soft coating
4	MoSi <sub>2</sub> < 5 microns	-	30 tsi	1500°C 2 hrs.	Adherent hard coating
5	MoSi <sub>2</sub> < 15 microns	SrZrO <sub>3</sub> < 15 microns	30 tsi	1500°C 2 hrs.	Non-adherent soft coating
6	MoSi <sub>2</sub> < 15 microns on sintered Mo barrier coating	SrZrO <sub>3</sub> < 15 microns	30 tsi	1500°C 2 hrs.	Non-adherent soft coating
7	MoSi <sub>2</sub> < 15 microns, 5% solids in dispersion	-	30 tsi	1400°C 1 hr.	Adherent with fair density
8	MoSi <sub>2</sub> < 15 microns, 1% solids in dispersion	-	30 tsi	1400°C 1 hr.	Non-adherent with high density
9	MoSi <sub>2</sub> < 5 microns, 1% solids in disper- sion, on sintered MoSi <sub>2</sub> bond layer	ZrO <sub>2</sub> (CaO stabilized) milled 6 hours	30 tsi	1400°C 1 hr.	Adherent with fair density and hardness
10	MoSi <sub>2</sub> < 5 microns, 1% solids in disper- sion, no MoSi <sub>2</sub> bond layer.	ZrO <sub>2</sub> (CaO stabilized) milled 6 hours	30 tsi	1400°C 1 hr.	No-adherent
11	No. 9 refired	-	30 tsi	1700°C 1 hr.	Adherent with good density and high hardness

2. Solids concentration:

1% vs 5% solids concentration of  $\text{MoSi}_2$  in the initial inter-metallic dispersion.

3. Barrier or undercoat layers:

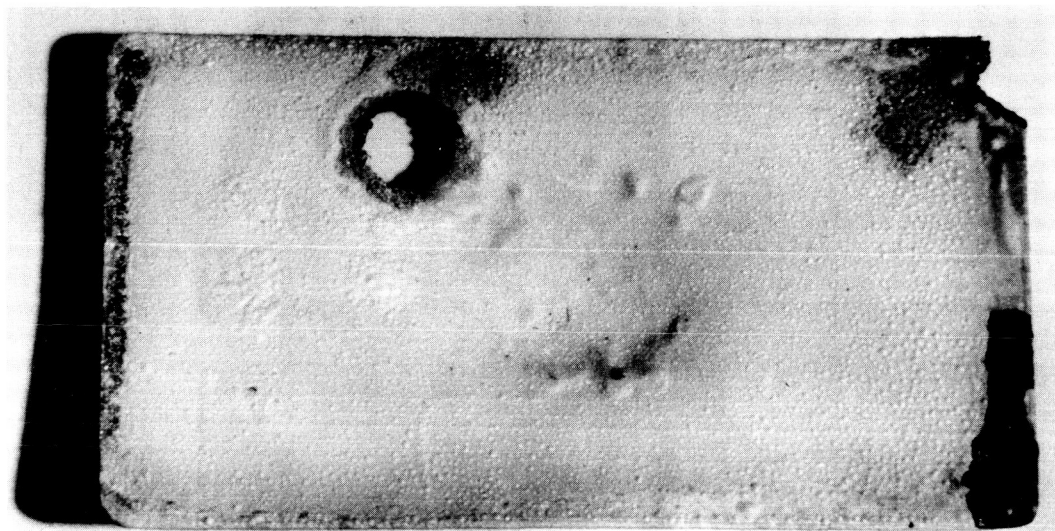
The effect of a sintered Mo or  $\text{MoSi}_2$  layer under the gradated coatings.

The data shown in Table 16 indicate that adherent coatings on Ta-10W can be produced from  $\text{MoSi}_2$  which has a particle size of 5 microns or less, and that a thin layer of  $\text{MoSi}_2$  which is sintered on the Ta-10W substrate will bond to the subsequent gradated coating. Secondly, it was found advisable to deposit from 5% rather than 1%  $\text{MoSi}_2$  dispersions since improved adherence was obtained.

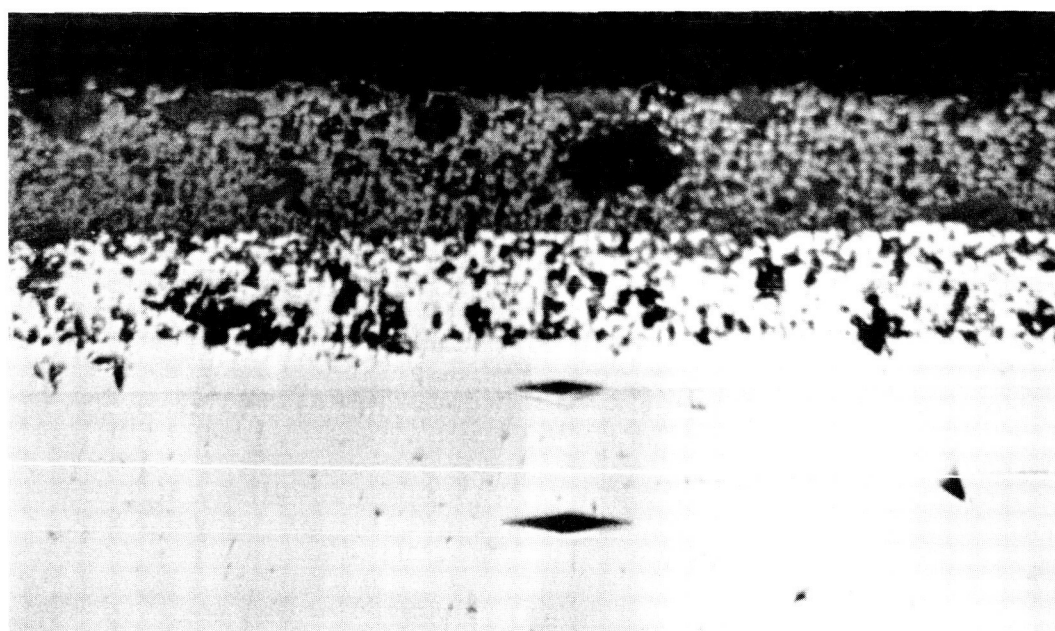
It was found that an acceptable procedure for obtaining adherent  $\text{MoSi}_2$ - $\text{ZrO}_2$  gradated coatings was to electrophoretically deposit and sinter a base coat of  $\text{MoSi}_2$  prior to the deposition of the  $\text{MoSi}_2$ - $\text{ZrO}_2$  gradated system. The base coat was deposited at 100 volts for 1-1/2 minutes, after which it was isostatically pressed at 30 tsi and sintered in argon at  $1400^\circ\text{C}$  for one hour. A gradated coating of  $\text{MoSi}_2$ - $\text{ZrO}_2$  was then applied to the  $\text{MoSi}_2$ -coated Ta-10W substrate.

The gradated coatings were isostatically densified at 30 tsi and sintered at  $1400^\circ$  to  $1700^\circ\text{C}$  for two hours in an argon atmosphere. The coatings heated at  $1400^\circ\text{C}$  were only presintered. Those sintered at  $1600^\circ$  and  $1700^\circ\text{C}$  were improved in density and adherence, and had a hard glass-like surface. Some porosity, however, was still evident in the gradated layer.

Oxidation tests at  $3000^\circ\text{F}$  were conducted on the  $\text{MoSi}_2$ - $\text{ZrO}_2$  specimens. Failure occurred almost immediately on specimens which were prepared by sintering at  $1400^\circ\text{C}$ . The specimens prepared by sintering at  $1600^\circ\text{C}$  survived 15 - 20 minutes before oxidation effects could be noticed. A photograph of an oxidized specimen is shown in Figure 21.



9x



$\text{ZrO}_2\text{-MoSi}_2$   
Gradated Layer

$\text{MoSi}_2$  Bond Layer

Substrate

400x

FIGURE 21

$\text{MoSi}_2\text{-ZrO}_2$  GRADATED COATING ON Ta-10W SPECIMEN  
AFTER OXIDATION AT  $1600^\circ - 1650^\circ\text{C}$  FOR 20 MINUTES

## 4.2 WSi<sub>2</sub>-Refractory Oxide Systems

Preliminary studies were made with several gradated coating systems containing WSi<sub>2</sub> deposited on Ta-10W substrates. The primary objective of this work was to determine the effect of sintering temperature on the structure of the coating, and to promote the development of non-porous surfaces for improved oxidation resistance. The gradated coating systems studied and the results of sintering experiments are shown in Table 17.

These experiments indicated that an increase in sintering temperature to 1700°C was beneficial in increasing the densities of the WSi<sub>2</sub>-CaZrO<sub>3</sub> and WSi<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> (MgO) gradated coatings. However, the density of the WSi<sub>2</sub>-ZrO<sub>2</sub> (CaO) gradated coating was still below 90% of theoretical, and the 1700°C temperature used was apparently still too low by several hundred degrees for complete sintering of the very refractory ZrO<sub>2</sub> component.

Specimens with and without a presintered base coat of WSi<sub>2</sub> were included in static oxidation tests at 1650°C. The only specimen which exhibited any degree of oxidation resistance was one which had a presintered base coat of WSi<sub>2</sub>-CaZrO<sub>3</sub>. It was removed from the furnace after eight minutes exposure to static air at 1650°C. Photographs of the surface and a cross section of this specimen are shown in Figure 22. Evidently the CaZrO<sub>3</sub> surface material fused with the WSi<sub>2</sub> during the oxidation test, produced a tight surface and thus afforded some protection. The appearance of the surface, however, indicates that free tungsten was available in the coating. The oxidation of this free metal apparently hastened the breakdown of the protective coating. Subsequent coatings were therefore siliconized to remove free tungsten as described in Section 3.3.

Specimens of four different gradated coating systems, i. e.,

1. CaZrO<sub>3</sub>-WSi<sub>2</sub>
2. Al<sub>2</sub>O<sub>3</sub>(4 MgO)-WSi<sub>2</sub>
3. (ZrO<sub>2</sub>-2% TiO<sub>2</sub>)-WSi<sub>2</sub>
4. (ZrO<sub>2</sub>-5% Al<sub>2</sub>O<sub>3</sub>)-WSi<sub>2</sub>

were coated, sintered and oxidation tested. All specimens were prepared



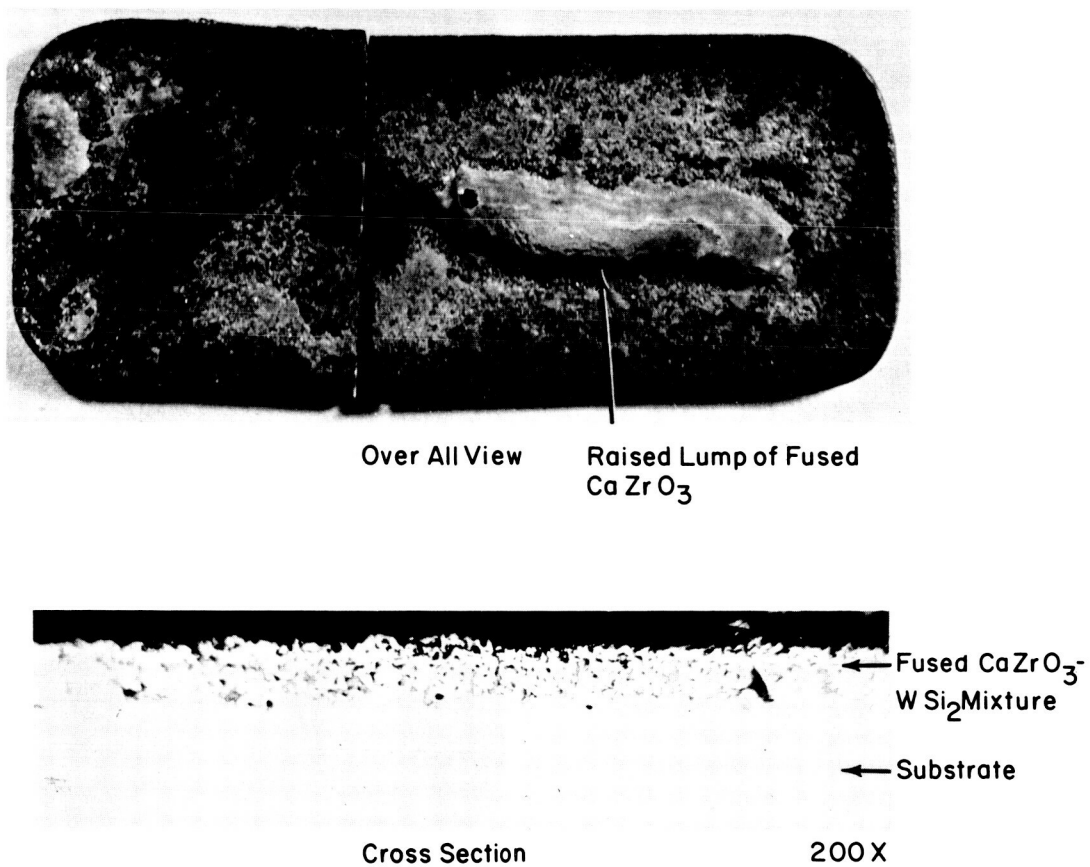


FIGURE 22  
OVER-ALL VIEW AND CROSS SECTION OF A  $\text{WSi}_2$  -  $\text{CaZrO}_3$   
GRADATED COATING ON Ta-10W AFTER EXPOSURE  
TO STATIC AIR AT 1650°C FOR 8 MINUTES

TABLE 17  
SINTERING RESULTS ON GRADATED COATINGS

Gradated Coating System	Deposition Data	Sintering Temp	Sintering Time	Results
WSi <sub>2</sub> -ZrO <sub>2</sub> (CaO)		1600°C	1 hr.	Coating semi-hard, porous.
WSi <sub>2</sub> -CaZrO <sub>3</sub>		1600°C	1 hr.	Coating hard, dense, reduced and cracked off substrate.
WSi <sub>2</sub> -ZrO <sub>2</sub> (CaO)	Grade - 55 sec - 100 volts ZrO <sub>2</sub> (CaO) - 45 sec - 150 volts ZrO <sub>2</sub> (CaO) - 45 sec - 200 volts	1700°C	1 hr.	Coating harder than that fired at 1600°C but still porous and cracked off substrate.
WSi <sub>2</sub> -CaZrO <sub>3</sub>	Grade - 55 sec - 100 volts CaZrO <sub>3</sub> - 45 sec - 150 volts CaZrO <sub>3</sub> - 45 sec - 200 volts	1700°C	1 hr.	Coating hard and dense but cracked off substrate.
WSi <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub> (MgO)	Grade - 50 sec - 100 volts Al <sub>2</sub> O <sub>3</sub> - 45 sec - 150 volts Al <sub>2</sub> O <sub>3</sub> - 45 sec - 200 volts	1700°C	2 hrs.	Coating hard and quite dense, adherent. Shrinkage cracks at one end of panel.

by depositing  $\text{WSi}_2$  onto a sandblasted and etched Ta-10W panel, densifying, sintering in argon at  $1400^\circ\text{C}$ , and siliconizing at  $1350^\circ\text{C}$ - $1375^\circ\text{C}$  to yield a 1.5-2.0 mil-thick  $\text{WSi}_2$  layer. Next, the desired gradated coatings were deposited onto the  $\text{WSi}_2$ , densified, sintered at  $1600^\circ\text{C}$ , and siliconized at  $1375^\circ\text{C}$ . For comparison purposes, a few specimens were prepared without siliconizing the gradated portion of the coating.

The specimens were oxidation tested in static air as shown in Table 18 which summarizes test conditions and results. A study of the results of these oxidation tests indicated that the best protection was obtained with the  $\text{Al}_2\text{O}_3(\text{MgO})\text{-WSi}_2$  and  $(\text{ZrO}_2\text{-}2\% \text{TiO}_2)\text{-WSi}_2$  coatings. Judging from post-test appearance, both types were either solid or very viscous liquids at the test temperature. In both coatings, gas bubbles were apparent under the surface. The cause of these bubbles was not determined.

The specimens used for oxidation tests at  $3200^\circ\text{F}$ - $3500^\circ\text{F}$  were prepared the same as the samples used in the  $2900^\circ\text{F}$ - $3000^\circ\text{F}$  tests, with the exception that the siliconization procedure was improved by heat-treating the silicon-coated specimen for 16 hours at  $1300^\circ\text{C}$  in vacuum rather than in argon. The vacuum siliconization was performed after the gradated coating was sintered on to the specimens.

In the first series of high temperature oxidation tests, four types of coated Ta-10W specimens were prepared as follows:

1.  $(\text{ZrO}_2\text{-}2\% \text{TiO}_2)\text{-WSi}_2$  gradated coating
2.  $(\text{ZrO}_2\text{-}2\% \text{TiO}_2)\text{-WSi}_2$  gradated coating with a presintered  $\text{WSi}_2$
3.  $\text{Al}_2\text{O}_3(\text{MgO})\text{-WSi}_2$  gradated coating
4.  $\text{Al}_2\text{O}_3(\text{MgO})\text{-WSi}_2$  gradated coating with a presintered  $\text{WSi}_2$  subcoat.

Ta-10W panels with  $(\text{ZrO}_2\text{-}2\% \text{TiO}_2)\text{-WSi}_2$  gradated coatings were exposed to static air at  $3200^\circ\text{F}$ . The results for these specimens (No's. 1 through 10) are shown in Table 19. They indicate that a  $\text{WSi}_2$  base coat coupled with a siliconizing treatment of the  $\text{WSi}_2\text{-ZrO}_2/\text{TiO}_2$  composite is a promising system for use at this test temperature, and that the life of this

TABLE 18

RESULTS OF OXIDATION TESTS ON Ta-10W SPECIMENS  
HAVING GRADATED OXIDE-INTERMETALLIC COATINGS

Gradated Coating	Specimen No.	Siliconizing Treatment	Oxidation Temperature	Results
CaZrO <sub>3</sub> -WSi <sub>2</sub>	1	Yes	2912°F	Removed after short time exposure. Surface bubbly and glassy, yellow. Specimen otherwise intact.
	2	Yes	2912°F	Removed after short time exposure. Coating on leading edge deteriorated on entrance to hot zone.
	3	Yes	2912°F	Removed after 10 minutes exposure. Yellow glassy reacted surface, uneven. Movement and flow of material noted during exposure.
Al <sub>2</sub> O <sub>3</sub> (MgO)-WSi <sub>2</sub>	1	Yes	2912°F	Removed after 30 minutes exposure. Surface dark, glassy and wrinkled. Failure site at bottom center where in contact with ZrO <sub>2</sub> setter pellet. No edge failure.
	2	Yes	2912°F	Removed after 30 minutes exposure. Surface dry. Failure at end and patch areas.
	3	Yes	3000°F	Removed after 5 minutes exposure. Failure at one corner.
Comments: This coating system was selected for further study because the surface appears to have a high density and high viscosity and the resistance to oxidation (30 minutes) was second best of the four systems studied.				
(ZrO <sub>2</sub> -2%TiO <sub>2</sub> )-WSi <sub>2</sub>	1	No	2950°F	Removed after 10 minutes exposure. Coating dark, glassy. Failure at corners on both ends.
	2	Yes	3000°F	Removed after 45 minutes exposure. Tight, glassy, adherent coat of yellow cast. Small bubbles on surface. Failure on underside where in contact with ZrO <sub>2</sub> setter pellet.

TABLE 18 (Continued)

Gradated Coating	Specimen No.	Siliconizing Treatment	Oxidation Test Temperature	Results
(ZrO <sub>2</sub> -2%TiO <sub>2</sub> )-WSi <sub>2</sub>	3	No	3000°F	Removed after 30 minutes exposure. Failure on one edge and at patch spot.
	4	No	3000°F	Removed after 10 minutes exposure. Failure at ends where in contact with Al <sub>2</sub> O <sub>3</sub> setter plate. Remainder of surface did not fail and coating had good adherence.
Comments: This coating system was selected for further study because of the high density and viscosity of the surface and because it had the best oxidation resistance of the four systems studied.				
(ZrO <sub>2</sub> -5%Al <sub>2</sub> O <sub>3</sub> )-WSi <sub>2</sub>	1	No	2912°F	Removed after short time exposure. Extreme failure.
	2	Yes	3000°F	Removed after short time exposure. Failure on bottom surface from center to edge.

TABLE 19  
RESULTS OF STATIC AIR OXIDATION TESTS  
ON COATED Ta-10W TEST SPECIMENS

Specimen No.	Type of Gradated Coating	Test Temp. (°F)	Time of Exposure (min)	Comments
1-1	(ZrO <sub>2</sub> . 2%TiO <sub>2</sub> )-WSi <sub>2</sub> , WSi <sub>2</sub> subcoat, siliconized	3200	75	Coating still protective. Outer ZrO <sub>2</sub> layer spalled. See Figure 21.
1-2	(ZrO <sub>2</sub> . 2%TiO <sub>2</sub> )-WSi <sub>2</sub> , WSi <sub>2</sub> subcoat, siliconized	3200	120	Coating still protective. Outer ZrO <sub>2</sub> layer spalled.
1-3	(ZrO <sub>2</sub> . 2%TiO <sub>2</sub> )-WSi <sub>2</sub> , WSi <sub>2</sub> subcoat, siliconized	3200	50	Coating failed between 30 and 50 minutes
1-4	(ZrO <sub>2</sub> . 2%TiO <sub>2</sub> )-WSi <sub>2</sub> , WSi <sub>2</sub> subcoat, siliconized	3200	155	Initial failure at patch spot. Coating protective up to 145 minutes exposure
1-5	(ZrO <sub>2</sub> . 2%TiO <sub>2</sub> )-WSi <sub>2</sub> , WSi <sub>2</sub> subcoat, siliconized	3200	120	Coating still protective. Same as Specimen No. 1-1
1-6	(ZrO <sub>2</sub> . 2%TiO <sub>2</sub> )-WSi <sub>2</sub> , WSi <sub>2</sub> subcoat, siliconized	3200	105	Coating still protective. Same as Specimen No. 1-1
1-5	(ZrO <sub>2</sub> . 2%TiO <sub>2</sub> )-WSi <sub>2</sub> , WSi <sub>2</sub> subcoat, siliconized	3200	120	Coating still protective. Same as Specimen No. 1-1
1-6	(ZrO <sub>2</sub> . 2%TiO <sub>2</sub> )-WSi <sub>2</sub> , WSi <sub>2</sub> subcoat, siliconized	3200	105	Coating still protective. Same as Specimen No. 1-1
2-7	(ZrO <sub>2</sub> . 2%TiO <sub>2</sub> )-WSi <sub>2</sub> , No subcoat, siliconized	3200	25	Specimen completely melted and disappeared
2-8	(ZrO <sub>2</sub> . 2%TiO <sub>2</sub> )-WSi <sub>2</sub> , No subcoat, siliconized	3200	9	Coating failed in several spots, including patch area. See Figure 22
2-9	(ZrO <sub>2</sub> . 2%TiO <sub>2</sub> )-WSi <sub>2</sub> , No subcoat, siliconized	3200	18	Coating failed at patch area
2-10	(ZrO <sub>2</sub> . 2%TiO <sub>2</sub> )-WSi <sub>2</sub> , No subcoat, siliconized	3200	8	Coating failed at patch area
3-11	ThO <sub>2</sub> -WSi <sub>2</sub> , WSi <sub>2</sub> subcoat, siliconized	3500	20, 18, 13	Coating failed at one spot on edge See Figure 23
3-12	ThO <sub>2</sub> -WSi <sub>2</sub> , WSi <sub>2</sub> subcoat, siliconized	3500	5	One end touched furnace wall. Coating failed at this end. Coating at other end still appears excellent. See Fig. 23
4-13	MgO-WSi <sub>2</sub> , WSi <sub>2</sub> subcoat, siliconized	3500	15	Coating reacted with ThO <sub>2</sub> setter. Specimen then melted
4-14	MgO-WSi <sub>2</sub> , WSi <sub>2</sub> subcoat, siliconized	3500	5	Coating failed on edges of one end and one side. See Figure 24
4-15	MgO-WSi <sub>2</sub> , WSi <sub>2</sub> subcoat, siliconized	3500	12	Coating failed at patch spot. Otherwise coating still protective
4-16	MgO-WSi <sub>2</sub> , WSi <sub>2</sub> subcoat, siliconized	3500	6	Coating failed on corners and one end

coating system at 3200°F is considerably reduced when the WSi<sub>2</sub> subcoat is not included. Photographs of the specimens after test at 3200°F are shown in Figures 23 and 24.

Static air oxidation tests at 3500°F were made on Ta-10W panel test specimens which were coated with gradated ThO<sub>2</sub>-WSi<sub>2</sub> and MgO-WSi<sub>2</sub>. Protective life for these coatings on the specimens tested was a maximum of 20 minutes, as indicated in Table 19.

Photographs of the specimens tested at 3500°F are shown in Figures 25 and 26.

Although the life in air at 3500°F was short, photographs of the tested specimens (Figures 24 and 25) show that oxidation occurred at single defect spots or at an edge, rather than as catastrophic overall failure. The photomicrographs illustrate good density, particularly in the ThO<sub>2</sub>-WSi<sub>2</sub> gradated coating on Ta-10W.

A final series of oxidation tests at 3500°F was performed on specimens coated with the ZrO<sub>2</sub>(3.5CaO)-WSi<sub>2</sub>, ZrO<sub>2</sub>(2TiO<sub>2</sub>)-WSi<sub>2</sub>, ThO<sub>2</sub>-WSi<sub>2</sub>, HfO<sub>2</sub>-WSi<sub>2</sub>, and Al<sub>2</sub>O<sub>3</sub>(4MgO)-WSi<sub>2</sub> coating systems. The results are listed in Table 20. Samples 2 and 3 of this series (corresponding to sample No's. 3-11 and 3-12, Table 19) represent the most promising coating system. The average life of this ThO<sub>2</sub>-WSi<sub>2</sub> system was estimated to be approximately 15 minutes at 3500°F which corresponds to an oxygen penetration rate of about 0.33 mil/min. for the normal 5 mil-thick coating.

A problem common to all coatings tested at 3500°F is interaction with the zirconia setter material. This reaction probably occurs between the silica formed during oxidation of the specimen and the setter, and might be alleviated by the use of other stable ceramic setters such as hafnia or thoria.

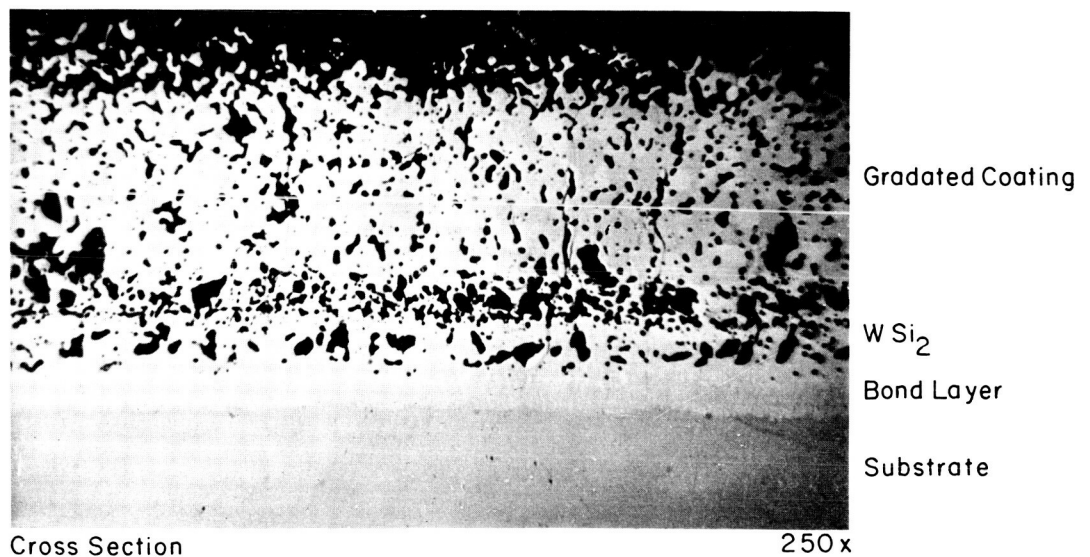
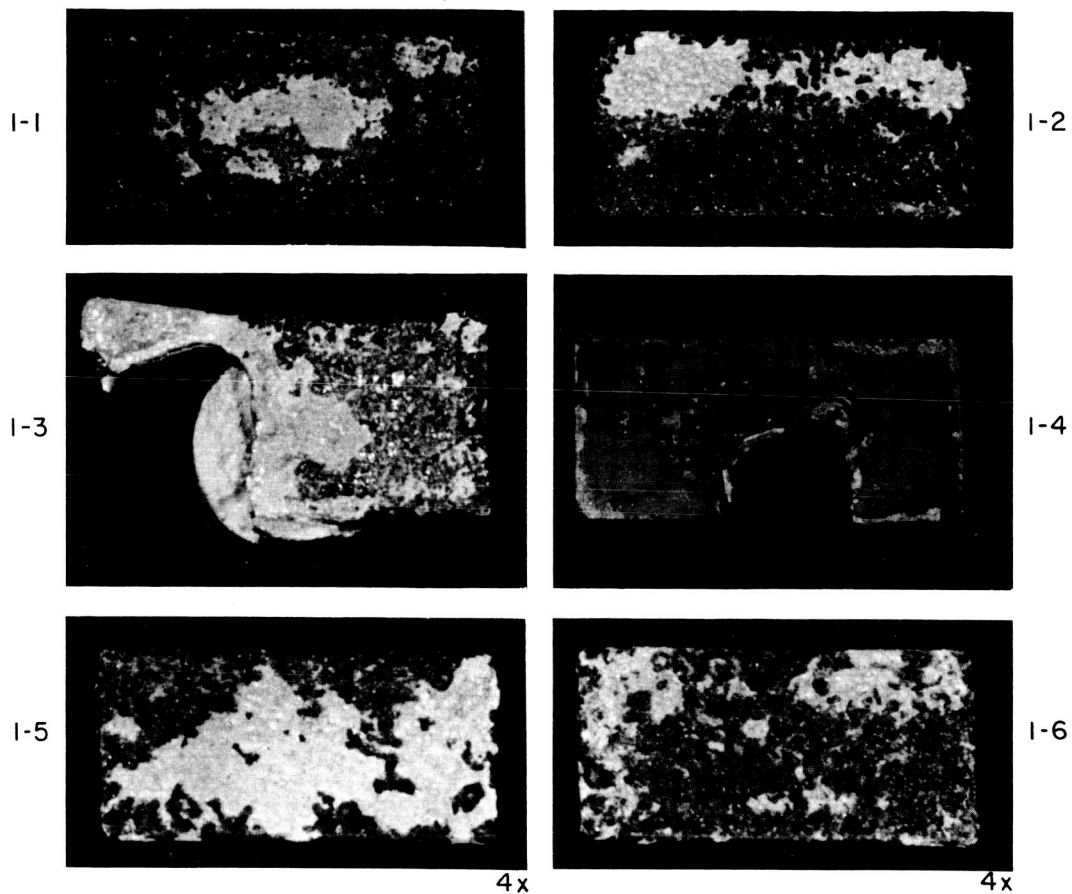


FIGURE 23

Ta-10W SPECIMENS AFTER STATIC AIR OXIDATION  
TEST AT 3200°F

Coating: Gradated ( $ZrO_2 \cdot 2\%TiO_2$ )- $WSi_2$

Subcoat:  $WSi_2$

Siliconization: 16 Hours, 1300°C, Vacuum



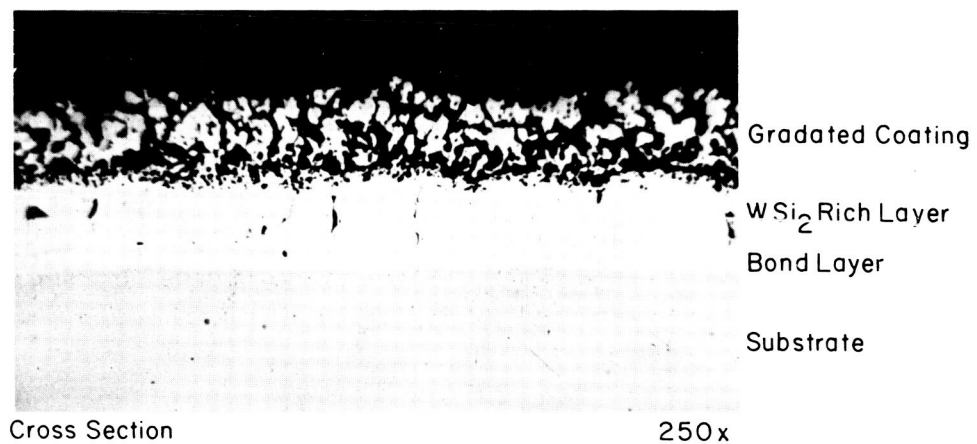
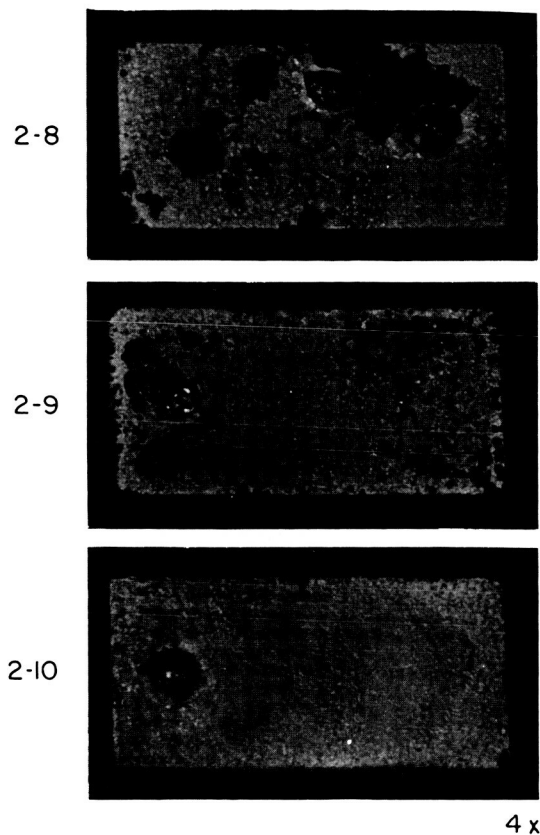


FIGURE 24

Ta-10W SPECIMENS AFTER STATIC AIR OXIDATION  
TEST AT 3200°F

Coating: Gradated ( $ZrO_2$ -2%  $TiO_2$ )- $WSi_2$

Subcoat: None

Siliconization: 16 Hours, 1300°C, Vacuum

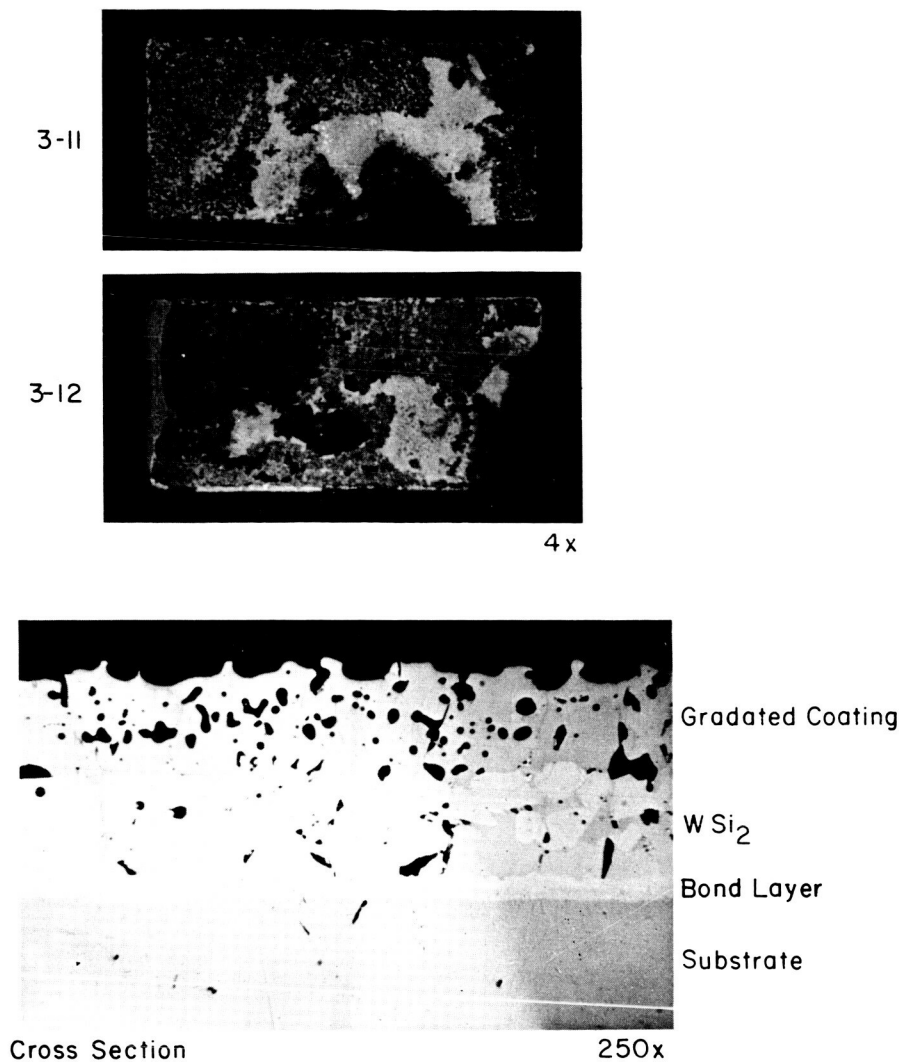
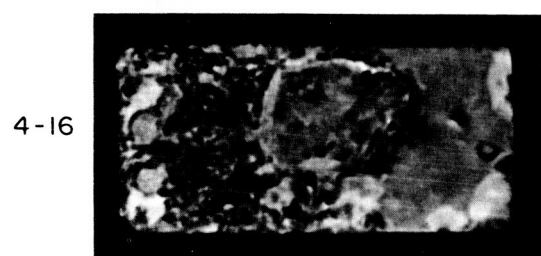
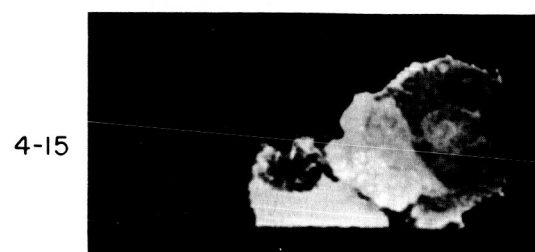
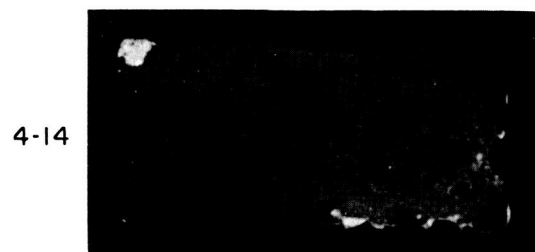
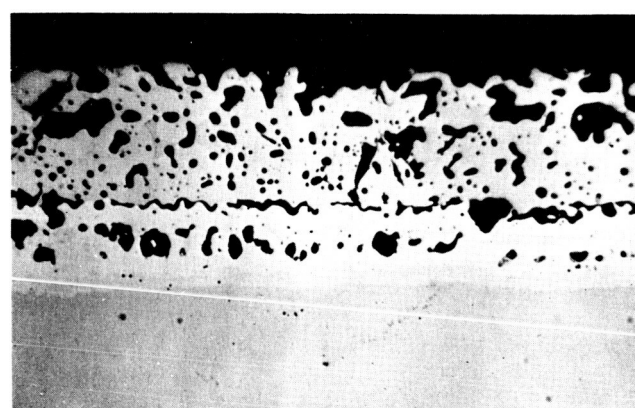


FIGURE 25  
Ta-10W SPECIMENS AFTER STATIC AIR OXIDATION  
TEST AT 3500°F

Coating: Gradated ThO<sub>2</sub>-WSi<sub>2</sub>  
Subcoat: WSi<sub>2</sub>  
Siliconization: 16 Hours, 1300°C, Vacuum



4 x



Gradated Coating

$WSi_2$   
Bond Layer

Substrate

Cross Section

250 x

FIGURE 26

Ta-10W SPECIMENS AFTER STATIC AIR OXIDATION  
TEST AT 3500°F

Coating: Gradated MgO- $WSi_2$

Subcoat:  $WSi_2$

Siliconization: 16 Hours, 1300°C, Vacuum

TABLE 20  
RESULTS OF STATIC AIR OXIDATION TESTS AT 3500°F  
ON COATED Ta-10W TEST SPECIMENS

<u>Specimen Number</u>	<u>Type of Gradated Coating</u>	<u>Exposure Time (Min.)</u>	<u>Comments</u>
00	ZrO <sub>2</sub> -WSi <sub>2</sub> , WSi <sub>2</sub> subcoat, siliconized	14	Initial failure at one spot on edge. Reaction with ZrO <sub>2</sub> (CaO) setter occurred.
0	Same as 00	4	Coating glassy and rough, and oxide appears reduced. Reaction with ZrO <sub>2</sub> (CaO) setter occurred.
1	(ZrO <sub>2</sub> ·2% TiO <sub>2</sub> )-WSi <sub>2</sub> , WSi <sub>2</sub> subcoat, siliconized	10	Coating glassy and rough. No specific failure although Ta <sub>2</sub> O <sub>5</sub> areas show on surface. Re- action with ZrO <sub>2</sub> (CaO) setter.
2	Same as 1	6	Initial failure at one corner. Coating reacted with ZrO <sub>2</sub> (CaO) setter.
3	ThO <sub>2</sub> -WSi <sub>2</sub> , WSi <sub>2</sub> subcoat, siliconized	13	Specimen appears intact. It was removed because of discoloration of surface during test. Reaction with ZrO <sub>2</sub> (CaO) setter.
4	Same as 3	18	Failure in spots. This was caused by re- action of coating with ZrO <sub>2</sub> (CaO) setter. Edges and surfaces not near setter are still excellent in appearance.
5	HfO <sub>2</sub> -WSi <sub>2</sub> , WSi <sub>2</sub> subcoat, siliconized	23	Primary failure: reaction with ThO <sub>2</sub> setter. Ends and edges still intact and covered with refractory HfO <sub>2</sub> coating.
6	Same as 5	3	Failed at one spot on edge and at patch area.
7	HfO <sub>2</sub> over ThO <sub>2</sub> -WSi <sub>2</sub> , WSi <sub>2</sub> subcoat, siliconized	17	Failed at one spot on edge. Coating rough and scale-like but still protective. Little or no reaction with ThO <sub>2</sub> setter.
8	HfO <sub>2</sub> over (ZrO <sub>2</sub> ·2TiO <sub>2</sub> )- WSi <sub>2</sub> , WSi <sub>2</sub> subcoat, siliconized	7	Specimen removed because portion of coating spalled. No oxidation of substrate however. No reaction with HfO <sub>2</sub> setter.
9	Al <sub>2</sub> O <sub>3</sub> (MgO)-WSi <sub>2</sub> , WSi <sub>2</sub> subcoat, siliconized.	2	Two corners failed, patch failed, Coating other- wise smooth and glassy. Al <sub>2</sub> O <sub>3</sub> grain setter.
10	Same as 9	7	End failure. Al <sub>2</sub> O <sub>3</sub> grain setter. Coating smooth and glassy.
11	Same as 9	5	Al <sub>2</sub> O <sub>3</sub> setter melted and reacted with coating.
12	Same as 9	13	Failure at patch only. Coating protective in other areas. Little or no reaction with HfO <sub>2</sub> setter.
13	Same as 9	10	Failure at patch spot only. HfO <sub>2</sub> setter. Similar to 12.
14	Same as 9	5	Similar to 12 and 13.

## 5. SUMMARY AND CONCLUSIONS

Electrophoretic deposition equipment was tested successfully for the preparation of 2-component, intermetallic compound-refractory oxide coatings which were continuously gradated in composition over a thickness of 4-8 mils. Although the equipment allowed close control of the relative volumetric throughput of two dispersions to a continuous flow coating cell, some variation in coating rates was observed among the various coating materials due to differences in their particle size distribution. An induction-heated, water-cooled, lampblack-insulated, zirconia tube furnace was assembled and utilized for oxidation tests at 3000°-4000°F.

A variety of boride, silicide, and aluminide intermetallic compounds were investigated as base coats to provide adherence of the gradated coating systems to Ta-10W alloy. Zirconium boride, "Boride-Z", and tantalum aluminide coatings diffused rapidly into the substrate when sintered at 1700°C and caused embrittlement of the alloy. Satisfactory adherence and minimum contamination was obtained with base coatings of TaSi<sub>2</sub>, WSi<sub>2</sub>, and MoSi<sub>2</sub>, when the average particle size of these coatings was reduced to approximately 10 microns. Sintering conditions were then studied for gradated overlay coatings of WSi<sub>2</sub>/ZrO<sub>2</sub>, MoSi<sub>2</sub>/ThO<sub>2</sub>, MoSi<sub>2</sub>/SrZrO<sub>3</sub>, and analogous systems, on base coats of MoSi<sub>2</sub> and WSi<sub>2</sub>. The oxide phase of these coating systems could be only partially sintered at temperatures up to 1700°C. Relatively dense outer coatings were obtained, however, by adding a second phase activator to the oxide component. Typical oxide systems of this type included ZrO<sub>2</sub>(stabilized)-2%TiO<sub>2</sub>, ThO<sub>2</sub>-SiO<sub>2</sub>, and Al<sub>2</sub>O<sub>3</sub>-4MgO.

Typical oxidation lives observed for the gradated coatings over a WSi<sub>2</sub> subcoat were:

WSi<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>-4MgO, WSi<sub>2</sub>/ThO<sub>2</sub>, WSi<sub>2</sub>/ZrO<sub>2</sub>-2TiO<sub>2</sub>, WSi<sub>2</sub>/MgO - 15 min.  
@ 3500°F

WSi<sub>2</sub>/ZrO<sub>2</sub>-2TiO<sub>2</sub> - 120 min. @ 3200°F

The average life of 15 minutes at 3500°F which was obtained for many systems corresponds to an approximate oxygen penetration rate through the coating of 0.33 mil/min. Most of the failures after 15 minutes were due to edge or corner defects or to interaction with the setter material,

and none of the coatings was observed to fail catastrophically. In view of these results, the gradated oxide- $\text{WSi}_2$  coatings are considered very promising for the protection of tantalum alloys from oxidation of temperatures of  $3500^\circ\text{F}$  and above.

Further optimization of the density of the oxide gradated coatings is required to improve their performance. These studies should include:

- a) Effect of particle size distribution, sintering time, and temperature on density and oxidation resistance of the gradated coating.
- b) Effect of  $\text{WSi}_2$ /oxide ratio on density and oxidation rate.
- c) Effect of relative thicknesses of base coat, gradated zone, and outer oxide coating on the protectiveness of the coating systems.
- d) Identification of stable setter materials for oxidation testing at  $3500^\circ\text{-}4500^\circ\text{F}$ .

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